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JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY

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Vol.
15
1960

LIST OF CONTENTS

NUMBERS 1/2

J. E. GINDLER, K. F. FLYNN and J. GRAY, JR.: Thermal neutron fission cross-section of ^{229}Th . 1
C. J. ORTH and R. K. SMITH: Short-lived isotopes of Nb and Zr from fission 4
I. G. ALMEIDA and L. MARQUEZ: A method for the enrichment of radioisotopes produced by (γ, n) 18
J. MACKIN, P. ZIGMAN, D. LOVE, D. MACDONALD and D. SAM: Radiochemical analysis of individual fall-out particles 20
I. G. CAMPBELL: The effect of amine scavengers on products of neutron irradiation of organic halides 37
I. G. CAMPBELL: Some properties of the unstable intermediate produced by isomeric transition or (n, γ) reaction in bromates 46
H. YAMATERA: Charge-transfer spectra in metal complexes, especially in halogenopentammine-cobalt(III) ions 50
R. H. HOLM and F. A. COTTON: Dipole moments and structures of some *bis*-(trifluoroacetylacetonato) complexes 63
R. E. PANZER and J. F. SUTTLE: Solvates of uranium tetrachloride with phosphorus oxychloride . 67
N. D. PESCHKO and B. P. BLOCK: The thermal stability of metal ammines—I. Pentamminechloro-chromium(III) chloride 71
L. R. OCONE, J. R. SOULEN and B. P. BLOCK: The thermal stability of metal ammines—II. Cobalt(II) and cobalt(III) compounds 76
W. B. WITMER and R. A. ZINGARO: Some new bromine–amine complexes 82
B. J. AYLETT: The silyl group as an electron acceptor—III. The relative stabilities of some complexes of silyl iodide with ethers and thioethers 87
T. D. SMITH: The salts of organic phosphorus acids—II. The infra-red spectra of salts of di-alkyl phosphites 95
D. SEYFERTH and H. P. KÖGLER: Preparation of organosilicon-substituted borazenes 99
M. H. MACDONALD and R. D. HILL: The products of electrolysis of sodium amide–potassium amide eutectic mixture 105
G. GIBSON, C. D. BEINTEMA and J. J. KATZ: The reaction of uranium oxides with dinitrogen pentoxide 110
V. CAGLIOTI, L. CIAVATTA and A. LIBERTI: Complexity of titanium(IV) fluoride solutions . . 115
C. V. BANKS and R. S. SINGH: Composition and stability of some metal-5-sulphosalicylate complexes 125
H. BUCHWALD and E. RICHARDSON: Molybdic acid and its organic complexes—IV. Complexes of molybdate with polyhydric phenols—a spectrophotometric study 133
F. NELSON, R. A. DAY, JR. and K. A. KRAUS: Anion exchange studies—XXX. A number of elements in ethylenediaminetetraacetic acid solutions 140
N. M. ISAAC, J. W. WILKINS and P. R. FIELDS: Separation of *trans*-curium elements from large quantities of curium, by liquid–liquid extraction 151
H. IRVING and D. N. EDGINGTON: Synergic effects in the solvent extraction of the actinides—I. Uranium(VI) 158
M. TAUBE: The influence of diluent polarity on the extraction of neptunium and uranium compounds to organic media 171
J. KORKISCH und F. TERA: Ionenaustausch in Lösungsmittelgemischen—III. Über die Verteilung des Thoriumchlorids zwischen seinen alkoholischen Salzsauren Lösungen und stark basischen Anionen-austauschern 177

Notes:

E. L. MUETTERTIES: Anomalous acceptor behaviour of boron tri-iodide 182
G. S. PANSON and C. E. WEILL: The action of $NaBH_4$ on $NaHSO_3$ 184
D. B. MCWHAN, J. C. WALLMANN, B. B. CUNNINGHAM, L. B. ASPREY, F. H. ELLINGER and W. H. ZACHARIASEN: Preparation and crystal structure of americium metal 185
C. W. F. T. PISTORIUS: The infra-red spectrum of $Th(OH)_4$ 187
E. KÖRÖS, E. SCHULEK and L. PATAKI: Contributions to the solvent effect in the iodine–iodoanti-pyrine exchange reaction 188
RILEY SCHAEFFER: Interconversion of boranes—III. An analysis of the "first stable intermediate" problem 190
R. A. Y. JONES and A. R. KATRITZKY: A correlation between the degree of ionization of phosphates and the frequency of phosphorus magnetic resonance 193
M. LINDNER, K. V. MARSH, J. A. MISKEL and R. J. NAGLE: The half-life of ^{181}Hf 194
ROBERT A. NAUMANN, MAYNARD C. MICHEL and JOHN L. POWER: Preparation of long-lived holmium-163 195

Letters to the Editor:

J. J. C. SCHATS and A. H. W. ATEN, JR.: Dipyridine complexes of astatine salts 197
A. H. W. ATEN, JR., J. G. VAN RAAPHORST, G. NOOTEBOOM and G. BLASSE: Coprecipitation of astatine iodide with solid iodine 198
L. H. BRIXNER: Structure and electrical properties of some new rare earth arsenides, antimonides and tellurides 199

Book Reviews:

LOUIS GORDON, MURRELL L. SALUTSKY and HOBART H. WILLARD: "Precipitation from Homogeneous Solution" (reviewed by DONALD F. PEPPARD) 202
J. K. DAWSON and G. LONG: "Chemistry of Nuclear Power" (reviewed by G. R. HALL) . . 202

Errata:

JOHN A. PANONTIN, ALBERT K. FISCHER and EDWARD A. HEINTZ: The preparation of mononitrato-dioxovanadium(V), VO_2NO_3 204

NUMBERS 3/4

F. D. S. BUTEMENT and P. GLENTWORTH: New radioactive isotopes of the rare earth elements . 205
J. H. FORREST, S. J. LYLE, G. R. MARTIN and J. J. MAULDEN: The uranium Z/uranium X_2 branching ratio 210
R. F. DOERING, W. D. TUCKER and L. G. STANG, JR.: A rapid method for the detection of ^{90}Sr contamination in ^{90}Y 215

J. ALSTAD and A. C. PAPPAS: Radiochemical studies of fission product lanthanum and lanthanides—I. Isolation of trace lanthanides using non-isotopic carrier and drop elution technique . . . 222
RUSSELL S. DRAGO: On the electronegativities of the Group IV elements 237
G. GIACOMETTI and A. TURCO: Tetra-co-ordination of nickel (II)—III. Visible and ultra-violet absorption spectra of $NiX_2{\cdot}2PR_3$ complexes 242
M. T. BECK: Catalysis of complex formation reactions 250
R. F. WILSON and F. L. JOE, JR.: Interaction of ruthenium(III) chloride solution with 1,2,3-benzotriazole 255
T. MOELLER, V. GALASYN and J. XAVIER: Observations on the rare earths—LXXII. The preparation and characterization of anhydrous and N,N-dimethylformamide-solvated acetates 259
E. GIESBRECHT: Phosphates and polyphosphates of the rare earth elements—III. Cerium(III) tripolyphosphates 265
J. MAGEE and E. RICHARDSON: Some studies on vanadic acid 272
J. W. PALMER and FRED BASOLO: Effect of transition metal ion on rates of hydrogen exchange in metal ammines 279
D. O. DEPREE, E. B. OLDENBURG and J. A. BURNS, JR.: The preparation of sodium cyanate by the reaction of sodium metal with urea 287
JAMES D. RAY: Potassium nitrite: Preparation and thermometric analysis 290
R. E. MCCARLEY and J. W. RODDY: The hydrogen–vanadium(V) oxytrichloride reaction . . . 293
A. D. KIRSHENBAUM, J. A. CAHILL and C. S. STOKES: The density of molten metal fluorides in the range of 1600°–2500°K 297
A. KANT and W. J. MCMAHON: Thermal decomposition of nitrogen-15 labelled hydrazine . . . 305
J. A. DUPONT and RILEY SCHAEFFER: Interconversion of boranes—I. A kinetic study of the conversion of tetraborane-10 to pentaborane-11 310
K. BORER, A. B. LITTLEWOOD and C. S. G. PHILLIPS: A gas–chromatographic study of the diborane pyrolysis 316
T. N. WATERS: Some investigations in the zirconium tetrafluoride–water system 320
J. O. EDWARDS and V. ROSS: Structural principles of the hydrated polyborates 329
M. ROSS and H. T. EVANS, JR.: The crystal structure of cesium biuranyl trisulphate, $Cs_2(UO_2)_2(SO_4)_3$ 338
L. H. BRIXNER: Preparation and crystallographic study of some new rare earth compounds . . 352
L. H. BRIXNER: X-Ray study and electrical properties of the systems $SrMo_xZr_{(1-x)}O_3$ and $SrMo_xTi_{(1-x)}O_3$ 356
A. J. DARNELL: The free energy, heat and entropy of formation of thorium tetrafluoride . . . 359
D. F. PEPPARD and J. R. FERRARO: An infra-red study of the systems tri-n-butyl phosphate–HNO_3 and bis-(2-ethylhexyl)-phosphoric acid–HNO_3 365
T. FREUND: The kinetics of the reduction of permanganate by cyanide in basic solution . . . 371
G. R. CHOPPIN and A. CHATHAM-STRODE: Ion exchange behaviour of the actinide elements in hydrochloric acid 377

Notes:

MILTON KAHN and A. L. LANGHORST: A novel method for the preparation of carrier-free lead-212 384
L. LINDNER and G. HARBOTTLE: Chemical behaviour of phosphorus-32 recoils in crystalline disodium hydrogen phosphate 386
R. D. JOYNER, J. CEKADA, JR., R. G. LINCK and M. E. KENNEY: Diphenoxysilicon phthalocyanine 387
J. A. MATTERN: Comparison of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope effects in some reactions of hydrogen peroxide 388

A list of some of the papers to be published in future issues 390

AUTHOR INDEX

(B denotes Book Review; E denotes Erratum)

ALMEIDA, I. G. p. 18
ALSTAD, J. p. 222
ASPREY, L. B. p. 185
ATEN, JR., A. H. W. pp. 197, 198
AYLETT, B. J. p. 87
BANKS, C. V. p. 125
BASOLO, F. p. 279
BECK, M. T. p. 250
BEINTEMA, C. D. p. 110
BLASSE, G. p. 198
BLOCK, B. P. pp. 71, 76
BORER, K. p. 316
BRIXNER, L. H. pp. 199, 352, 356
BUCHWALD, H. p. 133
BURNS, JR., J. A. p. 287
BUTEMENT, F. D. S. p. 205
CAGLIOTTI, V. p. 115
CAHILL, J. A. p. 297
CAMPBELL, I. G. pp. 37, 46
CEKADA, JR., J. p. 387
CHATHAM-STRODE, A. p. 377
CHOPPIN, G. R. p. 377
CIAVATTA, L. p. 115
COTTON, F. A. p. 63
CUNNINGHAM, B. B. p. 185
DARNELL, A. J. p. 359
DAY, JR., R. A. p. 140
DEPREE, D. O. p. 287
DOERING, R. P. p. 215
DRAGO, R. S. p. 237
DUPONT, J. A. p. 310
EDDINGTON, D. N. p. 158
EDWARDS, J. O. p. 329
ELLINGER, F. H. p. 185
EVANS, JR. H. T. p. 338
FERRARO, J. R. p. 365
FIELDS, P. R. p. 151
FISCHER, A. K. p. 204(E)
FLYNN, K. F. p. 1
FORREST, J. H. p. 210
FREUND, T. p. 371
GALASYN, V. p. 259
GIACOMETTI, G. p. 242
GIBSON, G. p. 110
GIESBRECHT, E. p. 265
GINDLER, J. E. p. 1
GLENTWORTH, P. p. 205
GRAY, JR., J. p. 1
HALL, G. R. p. 202(B)
HARBOTTLE, G. p. 386
HEINTZ, E. A. p. 204(E)
HILL, R. D. p. 105
HOLM, R. H. p. 63
IRVING, H. p. 158
ISAAC, N. M. p. 151
JOE, JR., F. L. p. 255
JONES, R. A. Y. p. 193
JOYNER, R. D. p. 387
KAHN, M. p. 384
KANT, A. p. 305
KATRITZKY, A. R. p. 193
KATZ, J. J. p. 110
KENNEY, M. E. p. 387
KIRSHENBAUM, A. D. p. 297
KÖGLER, H. P. p. 99
KOREISCH, J. p. 177
KÖRÖS, E. p. 188
KRAUS, K. A. p. 140
LANGHORST, A. L. p. 384
LIBERTI, A. p. 115
LINCK, R. G. p. 387
LINDNER, L. p. 386
LINDNER, M. p. 194
LITTLEWOOD, A. B. p. 316
LOVE, D. p. 20
LYLE, S. J. p. 210
MACDONALD, D. p. 20
MACDONALD, M. H. p. 105
MACKIN, J. p. 20
MAGEE, J. p. 272
MARQUEZ, L. p. 18
MARSH, K. V. p. 194
MARTIN, G. R. p. 210
MATTERN, J. A. p. 388
MAULDEN, J. J. p. 210
MCCARLEY, R. E. p. 293
MCMAHON, W. J. p. 305
MCWHAN, D. B. p. 185
MICHEL, M. C. p. 195
MIKKEL, J. A. p. 194
MOELLER, T. p. 259
MUETTERTIES, E. L. p. 182
NAGLE, R. J. p. 194
NAUMANN, R. A. p. 195
NELSON, F. p. 140
NOGUEROM, G. p. 198
OCONE, L. R. p. 76
OLDENBURG, E. B. p. 287
ORTH, C. J. p. 4
PALMER, J. W. p. 279
PANONTIN, J. A. p. 204(E)
PANSON, G. S. p. 184
PANZER, R. E. p. 67
PAPPAS, A. C. p. 222
PATAKI, L. p. 188
PEPPARD, D. F. pp. 202(B), 365
PESCHKO, N. D. p. 71
PHILLIPS, C. S. G. p. 316
PIETORIUS, C. W. F. T. p. 187
POWER, J. L. p. 195
RAAPHORST, J. G. VAN p. 198
RAY, J. D. p. 290
RICHARDSON, E. pp. 133, 272
RODDY, J. W. p. 293
ROSS, M. p. 338
ROSS, V. p. 329
SAM, D. p. 20
SCHAEFFER, R. p. 190, 310
SCHATZ, J. J. C. p. 197
SCHULEK, E. p. 188
SEYFERTH, D. p. 99
SINGH, R. S. p. 125
SMITH, R. K. p. 4
SMITH, T. D. p. 95
SOULEN, J. R. p. 76
STANO, JR., L. G. p. 215
STOKES, C. S. p. 297
SUTTLE, J. F. p. 67
TAUBE, M. p. 171
TERRA, F. p. 177
TUCKER, W. D. p. 215
TURCO, A. p. 242
WALLMANN, J. C. p. 185
WATERS, T. N. p. 320
WEILL, C. E. p. 184
WILKINS, J. W. p. 151
WILSON, R. F. p. 255
WITMER, W. B. p. 82
XAVIER, J. p. 259
YAMATERA, H. p. 50
ZACHARIASEN, W. H. p. 17
ZEMAN, P. p. 20
ZINGARO, R. A. p. 82

Vol. 15 1960

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THERMAL NEUTRON FISSION CROSS-SECTION OF ^{229}Th*

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(*Received* 21 *October* 1959)

Abstract—The fission cross-section of ^{229}Th for thermal neutrons has been determined by counting samples placed in the thermal column of the Argonne heterogeneous heavy-water reactor, CP-5 Comparison of the fission counting rates of ^{229}Th samples with those of ^{235}U and ^{239}Pu standards gave a cross-section value of 30·5 ± 3 barns.

THE thermal neutron fission cross-section of ^{229}Th has been reported to be 45 barns within 25 per cent.[1] Preliminary work by the authors of this paper indicated the lower limit of the above value to be more nearly correct. The following is a description of an experiment designed to assign a more definitive value for this cross-section.

EXPERIMENTAL

Chemical separation

Thorium-229 was separated from its uranium parent, ^{233}U, by adsorption from a 1 M HNO_3 solution onto a cation exchange column and subsequent elution by means of a 0·5 M ammonium citrate solution at a pH of 6.† Following the initial separation the thorium was subjected to an extensive chemical purification to assure removal of any other fissionable elements that may have been present.

The citrate solution containing the thorium was evaporated with *aqua regia* to destroy the citrate and the thorium carried on a LaF_3 precipitate. This precipitate was converted to the hydroxide and dissolved in concentrated HCl containing a trace of HNO_3. This solution was then passed through a series of three Dowex A-1 anion exchange columns to adsorb any uranium and/or plutonium. The thorium contained in the column eluant was co-precipitated with LaF_3 and converted to the hydroxide. Upon dissolution with concentrated HCl the thorium was extracted with a 10 per cent solution of mono-octyl phosphate in toluene. For further purification from uranium the organic solution was scrubbed three times with concentrated HCl, once with a 1 M HNO_3–0·1 M $NaBrO_3$ solution and finally two more times with HCl.[2] The thorium was re-extracted with 4 M HF–0·5 M HCl solution after dilution of the organic phase with tri-butyl phosphate. Following evaporation of the fluoride solution to near dryness the thorium was dissolved in concentrated HCl containing a trace of HNO_3 and again passed through a series of three anion exchange columns. The eluant from the final column was evaporated just to dryness with HNO_3 and then taken up in 0·1 M HNO_3. A portion of this solution was extracted into a 0·2 M thenoyl trifluoroacetone (TTA)–benzene solution. Sample no. 1 was prepared by deposition of the TTA solution onto a platinum disk $\frac{1}{2}$ in. diameter and 0·005 in. thick. The disk was heated to redness in an induction heater to remove the organic deposit.

The remainder of the thorium was further purified by repetition of some of the above procedures: a LaF_3 co-precipitation, conversion to the hydroxide and passage through another series of three anion exchange columns, co-precipitation with $La(OH)_3$, dissolution with 0·1 M HNO_3 and extraction with a TTA-benzene solution. A second sample (no. 2) was prepared from this TTA

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† The initial separation of thorium daughter—uranium parent was made several years prior to the present experiment.[2]

[1] M. H. STUDIER, A. GHIORSO, F. HAGEMANN, TID-5223 (Pt. 2) Paper No. 9.1 (1952).
[2] L. B. MAGNUSSON, Private communication (1952).
[3] D. F. PEPPARD, G. W. MASON and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **10**, 117 (1959).

solution. Sample no. 3 was prepared by stripping the thorium from the TTA–benzene solution with nitric acid and volatilizing it onto a masked platinum disk.

Fission measurements

The α-activity of ^{229}Th in each sample was determined by α-pulse analysis and total α-counting. The number of atoms of ^{229}Th was calculated from its α-activity, an α-half-life of 7340 years[4] and the α-counter efficiency.* The results of this calculation are given in Table 1.

Standard samples of ^{239}Pu and ^{233}U were prepared from stock solutions.† Mass spectrometric analyses of these solutions are given in Table 2. The number of atoms in each standard sample was calculated from the α-activity, the α-counter efficiency* and the half-life of the respective nuclide. A half-life of 24,360 years[6] was used for ^{239}Pu and $1{\cdot}626 \times 10^5$ years[7] for ^{233}U. These results are also given in Table 1.

TABLE 1.—DETERMINATION OF THE FISSION CROSS-SECTION OF ^{229}Th

Sample	Atoms of ^{229}Th	Net fissions (c.p.m.)	Standard	Atoms of standard	Net fissions (c.p.m.)	Approximate flux (neutrons^{1}cm^{-2}sec^{-1})	$\sigma_f(^{229}\text{Th})$ (barns)
1	$6{\cdot}70 \times 10^{13}$	48,500	^{233}U	$13{\cdot}85 \times 10^{12}$	175,400	$4{\cdot}0 \times 10^{11}$	30·1
	$6{\cdot}70 \times 10^{13}$	50,000	^{239}Pu	$8{\cdot}88 \times 10^{12}$	175,600	$4{\cdot}0 \times 10^{11}$	30·2
2	$6{\cdot}03 \times 10^{14}$	172,000	^{233}U	$13{\cdot}85 \times 10^{12}$	67,100	$1{\cdot}5 \times 10^{11}$	31·1
	$6{\cdot}03 \times 10^{14}$	171,600	^{239}Pu	$8{\cdot}88 \times 10^{12}$	64,700	$1{\cdot}5 \times 10^{11}$	31·3
3	$2{\cdot}92 \times 10^{14}$	211,500	^{233}U	$13{\cdot}85 \times 10^{12}$	176,100	$4{\cdot}0 \times 10^{11}$	30·0
	$2{\cdot}92 \times 10^{14}$	218,000	^{239}Pu	$8{\cdot}88 \times 10^{12}$	176,200	$4{\cdot}0 \times 10^{11}$	30·2
							Av. 30·5

TABLE 2.—MASS SPECTROMETRIC ANALYSIS OF STOCK SOLUTIONS USED TO PREPARE FISSION COUNTING STANDARDS

Solution	Nuclides	Per cent composition by mass
^{233}U	^{233}U	$98{\cdot}33 \pm 0{\cdot}02$
	^{234}U	$0{\cdot}127 \pm 0{\cdot}002$
	^{236}U	$0{\cdot}0102 \pm 0{\cdot}0004$
	^{238}U	$1{\cdot}53 \pm 0{\cdot}02$
^{239}Pu	^{239}Pu	$99{\cdot}972 \pm 0{\cdot}001$
	^{240}Pu	$0{\cdot}028 \pm 0{\cdot}001$
	^{241}Pu	$<0{\cdot}0007$

Fission measurements were made in the thermal column of the Argonne heavy-water pile, CP-5, using a double ionization chamber. The chamber permitted the counting of two samples, one of thorium and a standard, simultaneously. The two samples were placed back-to-back in the chamber

* Three total α-counters were used during the course of the experiment. The counting efficiency of one had been determined[5] to be 51·6 per cent for an ^{241}Am sample evaporated upon a platinum disk. The other two counters were intercalibrated with this counter using a plutonium standard. This intercalibration gave efficiencies of 50·6 per cent for the counter used for the thorium samples and 51·6 per cent for the counter used for both the ^{233}U and ^{239}Pu standards. The extent to which this intercalibration is correct assuming the counting efficiency for plutonium and the other nuclides is the same as that for ^{241}Am, determines in part the accuracy of the experiment.

† The stock solutions and standard plates were prepared by F. T. HAGEMANN.

[4] F. HAGEMANN, L. I. KATZIN, M. H. STUDIER, G. T. SEABORG and A. GHIORSO, *Phys. Rev.* **79**, 435 (1950)
[5] W. C. BENTLY. Private communication (1957).
[6] J. C. WALLMANN, Thesis, University of California Radiation Laboratory Report UCRL-1255 (1951) (unpublished).
[7] YA. P. DOKUCHAYEV and I. S. OSIPOV, *Atomnaya Energiya* **6**, 73, (1959).

Vol. 15 1960

perpendicular to the longitudinal axis of the thermal column such that the sample positioned nearest the core of the pile received a neutron flux 1·017 times greater than the other sample. Measurements were made at two flux positions, one of approximately 4×10^{11} neutrons cm^{-2}sec^{-1} and the other of approximately $1{\cdot}5 \times 10^{11}$ neutrons cm^{-2}sec^{-1}. The lower flux was used with the larger thorium sample (no. 2) to reduce the fission counting-rate to a level such that coincidence losses were less than 2 per cent.

The thermal nature of the neutrons had been determined previously by PFAFF and SHELTON[8] who measured the activities induced in bare and cadmium covered gold foils located at various positions in the column. The ratio of the activities of bare to covered gold foils was found to be $1{\cdot}2 \times 10^3$ and $1{\cdot}4 \times 10^3$ for the high and the low flux positions, respectively.

Background counting-rates determined with a blank platinum disk in the chamber were small compared to those obtained with either the thorium samples or the ^{233}U and ^{239}Pu standards. With the high neutron flux the background in chamber *A* was 270 c.p.m. and in *B* 133 c.p.m. With the low flux, chamber *A* had a background of 140 c.p.m. and *B* 74 c.p.m.

The fission counting-rates corrected for coincidence loss, sample position, and background are given in Table 1.

RESULTS

The fission cross-section of ^{229}Th for thermal neutrons has been calculated from the relation

$$\sigma_{Th} = \frac{F_{Th}}{N_{Th}} \cdot \frac{N_{std}\sigma_{std}}{F_{std}},$$

where N is the number of atoms of the fissioning nuclide and F is the fission counting rate with reference to thorium (Th) or standard (std).

Fission cross-section values of 527 barns[9] for ^{233}U and 746 barns[9] for ^{239}Pu were used. The latter cross-section was multiplied by a factor of 1·075[10] to correct for the fact that the ^{239}Pu fission cross-section is not 1/v in the thermal region and that the neutron distribution is assumed to be Maxwellian.

Table 1 lists the calculated fission cross-section of ^{229}Th for thermal neutrons for each of six measurements. The average value of this cross-section is 30·5 barns and has a precision of 0·5 barn. The absolute error is estimated to be less than 10 per cent or 3 barns. This includes errors in counting because of background, coincidence loss, sample position and counter efficiency as well as the statistical error, errors in the half-life determination of the various nuclides, and errors in the fission cross-section of the standards.

LEBEDEV and KALASHNIKOVA[11] have shown recently that slow neutrons with 0·5 eV to several tens of electron volts have a greater effect on the fission of ^{229}Th than they do on ^{235}U. In view of this it would be of great interest to determine the fission cross-section of ^{229}Th as a function of neutron energy.

Acknowledgements—The authors would like to thank Dr. L. B. MAGNUSSON for the ^{229}Th used in the experiment, Dr. F. T. HAGEMANN who furnished the standard samples, and Mr. D. J. HENDERSON who made the α-pulse analyses.

[8] E. R. PFAFF and R. D. SHELTON, *Wright Air Development Command* Technical Report 57-361, Vol.I, ASTIA Document No. AD 155789, Appendix III, pp. 707–729 (1958) (unpublished).
[9] D. J. HUGHES and R. B. SCHWARTZ, *Neutron Cross-sections*, Brookhaven National Laboratory Report BNL 325, (2nd Ed.), July, 1958 [Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. (1958)].
[10] D. J. HUGHES and J. A. HARVEY, *Neutron Cross-sections*, Brookhaven National Laboratory Report BNL-325, July, 1955 [Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. (1955)].
[11] V. I. LEBEDEV and V. I. KALASHNIKOVA, *Soviet Physics JETP* **35**, (8), 370 (1959).

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SHORT-LIVED ISOTOPES OF Nb AND Zr FROM FISSION*

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Abstract—The previously-reported nuclides ^{98}Nb, ^{99}Nb and ^{99}Zr, plus three other short-lived β-emitters tentatively identified as ^{100}Nb, ^{101}Nb and ^{98}Zr, have been observed in the Nb and Zr fractions rapidly separated from ^{235}U fission products. The properties observed are as follows. ^{98}Nb: $t_{1/2}$ = 51·5 ± 1·0 min; E_γ (MeV) = 0·330 ± 0·005, 0·720 ± 0·010, 0·780 ± 0·010, 1·16, 1·44, 1·52, 1·68, 1·88, 1·93, 2·24 and 2·7; $E_{\beta\,max}$ = 3·1 ± 0·2 MeV; Q_β = 4·6 ± 0·2 MeV. ^{99}Nb: $t_{1/2}$ = 2·4 ± 0·3 min; E_γ (MeV) = 0·100 ± 0·002, 0·260 ± 0·005. ^{99}Zr: $t_{1/2}$ = 35 ± 5 sec. ^{100}Nb: $t_{1/2}$ = 3·0 ± 0·3 min; E_γ (MeV) = 0·140 ± 0·005, 0·360 ± 0·010, 0·450 ± 0·010, 0·530 ± 0·010, 0·65, 2·2, 2·3, 2·65 and 2·8. ^{101}Nb: $t_{1/2}$ = 1·0 ± 0·2 min. ^{98}Zr: $t_{1/2} \sim 1$ min. A search was made for a low-spin isomer of ^{96}Nb by rapid β- and γ-counting of Zr samples which had been bombarded with 3·0–5·5 MeV protons. No activity attributable to such an isomer was observed. The low-spin isometric state, if it exists, has a half-life less than 5 sec.

ALTHOUGH the neutron-rich isotopes of Zr and Nb occur in the low-mass peak of the fission product yield distribution, those of mass 97 are the heaviest for which detailed decay information exists. Of those of mass >97, only ^{98}Nb, ^{99}Nb and ^{99}Zr have been identified. ^{98}Nb was first assigned by BOYD[1], who reported a 30 min Nb activity produced by deuteron bombardment of enriched ^{100}Mo; the reaction was assumed to be ^{100}Mo(d,α)^{98}Nb. DUFFIELD *et al.*[2] were the first to identify ^{99}Nb, which they produced by ^{100}Mo(γ,p). They reported a half-life of 2·5 min and, by aluminium absorption measurements, a maximum β-energy of 3·2 MeV. More recently, PAPPAS and THOMASSEN[3] have observed half-lives of 26 min for ^{98}Nb, 3·8 min for ^{99}Nb, and 30 sec for ^{99}Zr. TROUTNER[4], measuring fission yields of the Nb isotopes, observed a 51 ± 3 min activity which he assigned to ^{98}Nb after confirmation by the ^{98}Mo(n,p) reaction.

The present investigation was undertaken to:

(1) remeasure the half-lives of ^{98}Nb, ^{99}Nb and ^{99}Zr and obtain information on their radiations; (2) extend the search to heavier isotopes of Zr and Nb; (3) investigate the possibility of isomerism in ^{96}Nb.

EXPERIMENTAL

Source of fission products

Fission products were produced by irradiation of 93 per cent enriched ^{235}U as $UO_2(NO_3)_2 \cdot 6H_2O$ in the Los Alamos "water-boiler" reactor for periods of 20–60 sec in a neutron flux of 10^{12} cm^{-2} sec^{-1}. A pneumatic-transfer system was used to deliver the samples from the reactor to the radiochemistry laboratory, where they were caught in a trapping mechanism; chemical processing was started within 10 sec after the end of irradiation.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] G. E. BOYD, Oak Ridge National Laboratory Report ORNL-229 (1949).
[2] R. B. DUFFIELD, L. HSIAO and E. N. SLOTH, *Phys. Rev.* **79**, 1011 (1950).
[3] A. C. PAPPAS and J. A. THOMASSEN. Private communication (March 1958) cited by D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[4] D. E. TROUTNER. Thesis, Washington University, St. Louis, Missouri (1959).

Vol. 15 1960

Instrumentation

The data were obtained chiefly with β- and γ-scintillation spectrometers used in conjunction with the Los Alamos Model II 100-channel pulse-height analyser. A shielded 3 in. × 3 in. NaI(Tl) scintillator coupled to a 5 in. DuMont 6364 photomultiplier was used for most of the γ-spectra. γ-Ray photo-peak areas were converted to relative intensities by application of the detector efficiencies of HEATH[5]. For γ–γ coincidence work, a second scintillator unit with a $1\frac{1}{2}$ in. × $1\frac{1}{2}$ in. NaI(Tl) crystal was used. Coincidence measurements were made at both 90° and 180°, depending on whether or not back-scatter peaks would interfere with the interpretation of the spectrum under investigation. The coincidence circuit had a resolving time of 0·2 μsec.

The β-ray spectrum of ^{98}Nb was measured with a $\frac{5}{8}$ in. thick × $1\frac{5}{8}$ in. diameter *trans*-stilbene scintillator. The β-scintillation spectrometer was calibrated with the following sources: ^{32}P, ^{90}Y, ^{106}Ru–^{106}Rh and ^{144}Ce–^{144}Pr. The niobium pentoxide samples (~5 mg cm^{-2} thick) and the β-energy calibration sources were mounted on cardboard plates. ^{99}Mo β-counting was done with standard β-proportional counters.

The Los Alamos large Van de Graaff accelerator was used for the proton bombardment of Zr foil. The Zr foils were transferred manually from the beam tube to the detectors in about 10 sec.

The Los Alamos Cockcroft–Walton accelerator was used as the source of 14 MeV neutrons to produce the ^{98}Mo(n,p) reaction.

Chemical procedures

(1) *Separation of* Nb *from fission products.* The irradiated uranyl nitrate was dissolved in a few millilitres of water containing Nb^{5+} (in oxalic acid), Mo^{6+}, Te^{4+}, Te^{6+} and Zr^{4+} carriers. The Nb was precipitated as $Nb_2O_5{\cdot}xH_2O$ by the addition of 25 ml of hot concentrated HNO_3, the precipitate was centrifuged, and the filtrate was discarded. The $Nb_2O_5{\cdot}xH_2O$ was dissolved in hot concentrated HCl and the Nb was then extracted into di-isopropylketone as described by HICKS and GILBERT[6]. After the Nb was back-extracted into 6 F HCl, Mo and Te hold-back carriers were added and the Nb was then re-precipitated with NH_4OH. The precipitate was dissolved in hot concentrated HCl, Sb^{3+} carrier was added and the solution was made to 2 F HCl. Sb was precipitated with H_2S while Nb remained in solution. After final precipitation with NH_4OH in the presence of Mo and Te hold-back carriers, the Nb was ready for examination. This procedure could be carried out in 12 min with a radiochemical yield of ~30 per cent. Decontamination from Te activities could be achieved only if the hold-back carrier contained Te in both the 4+ and 6+ oxidation states.

(2) *Separation of* Zr *from fission products.* Two methods were used to separate Zr from fission products The first method was the slower of the two, but decontaminated the Zr very well. The other method gave a very fast separation with poorer decontamination.

In the first method, the irradiated uranyl nitrate was dissolved in 8 F HNO_3 and the solution was extracted with thenoyltrifluoroacetone (TTA) in xylene as described by MOORE[7]. The organic layer was washed once with 8 F HNO_3. The carrier-free Zr in the organic layer was then back extracted into 0·2 F HNO_3–0·2 F HF containing about 20 mg Zr carrier. Once the Zr had been back extracted, 10 mg of La carrier was added, and after removal of LaF_3 by centrifugation, excess Ba^{2+} was added to the supernate and the Zr was precipitated as $BaZrF_6$. This procedure required ~ 10 min and the radiochemical yield was ~ 20 per cent. Careful examination the following day showed no detectable contamination other than ^{99}Mo which had grown in from ^{99}Zr. Since the Zr separated by this procedure exhibited no activity in the half-life range 2 min to 17 hr, the half-life range <2 min was explored by recourse to a crude but faster Zr separation. The irradiated uranyl nitrate was dissolved in 1 F HCl in the presence of Te^{4+} carrier, and uranium was precipitated by the addition of excess NH_4OH. After centrifugation, the precipitate was dissolved in 6 F HCl and the solution was extracted with TTA. The TTA phase was washed once with 6 F HCl, separated, and transferred to a plastic cup for β-counting. Radiochemical examination of the liquid sample 19 hr later showed only a small amount of ^{99}Mo and ^{132}Te in addition to the very large ^{97}Zr fraction.

(3) *Milking of daughter activities from* Nb. After the initial precipitation of Nb as the hydrous oxide, as described in *Chemical procedures* (1), the precipitate was dissolved in a few drops each of

[5] R. L. HEATH, *Scintillation Spectrometry γ-Ray Spectrum Catalogue.* U.S.A.E.C. Research and Development Report IDO-16408 (1957).
[6] H. G. HICKS and R. S. GILBERT, *Analyt. Chem.* **26**, 1205 (1954).
[7] F. L. MOORE, *Analyt. Chem.* **28**, 997 (1956).

concentrated HNO_3 and HF, and an accurately-known 20 mg portion of Mo^{6+} carrier containing a few millilitres of Br_2 water was added to the solution. The Nb was precipitated with NH_4OH and the mixture was centrifuged. The supernate, which contained the Mo, was set aside for later analysis. The Nb was redissolved, new Mo carrier was added, and the procedure was repeated. Each precipitation cycle required 2 min. The time of Mo separation was recorded at the start of centrifugation. Separate control experiments showed that ~2 per cent of the Nb was lost in each cycle and ~1 per cent of the Mo activity was absorbed in the $Nb_2O_5 \cdot xH_2O$ for each cycle. The Mo from each cycle was later decontaminated carefully by two cycles involving scavenging with $Fe(OH)_3$ and precipitating with α-benzoinoxime in oxalic acid.

(4) *Milking of daughter activities from* Zr. The Zr fraction was separated from Nb and Mo fission products by precipitation of $Zr_3(PO_4)_4$ from 8 F H_2SO_4 containing 1 ml of concentrated H_3PO_4 in the presence of Nb and Mo carriers. Nb and Mo remained in the supernate when the mixture was centrifuged and were set aside for later analysis. The $Zr_3(PO_4)_4$ was dissolved in hot concentrated H_2SO_4, Nb and Mo carriers were again added and the solution was made to 8 F H_2SO_4 to reprecipitate $Zr_3(PO_4)_4$. This process was then repeated for several cycles, each cycle requiring 1·5 min. The time of each separation was recorded at the start of centrifugation. The Mo in the Nb–Mo fraction was later carefully decontaminated and the ^{99}Mo was β-counted.

This milking procedure was tested on ^{97}Zr by measurement of the ^{97}Nb in a series of Nb–Mo extracts. It yielded a ^{97}Zr half-life of 18 ± 2 hr, which compares favourably with the known value of 17 hr.

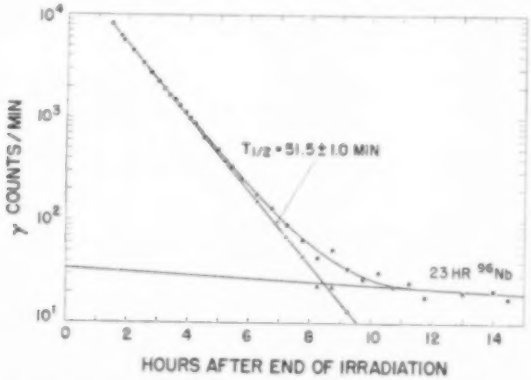

FIG. 1.—Early portion of the decay curve of the Nb scintillation γ-spectrum in the energy range 0·75 to 1·75 MeV.

EXPERIMENTAL RESULTS

I. ^{98}Nb

(a) *Half-life and mass assignment.* β-counts of Nb started within an hour after end of irradiation, decayed initially with an ~1 hr half-life which lengthened to 23 hr. Subtraction of the known 23 hr and 72 min periods of ^{96}Nb and ^{97}Nb, respectively, left a final component of ~50 min half-life. Since the relatively large amounts of the 72 min ^{97}Nb component in the β-decay curves made an accurate determination of the shorter period difficult, the half-life of the latter was obtained by γ-counting. For γ-counting, the gain and discriminator settings were adjusted to accept events only in the photopeak energy range 0·75 to 1·75 MeV, which excluded the 0·66 MeV γ-ray of ^{97}Nb. The resultant decay data, plotted in Fig. 1, showed components of half-life 51·5 ± 1·0 min and 23 hr.

The presence of a strong photopeak at 0·780 MeV, which agrees in energy with the first excited (2+) state of ^{98}Mo as determined by Coulomb excitation,[8] suggested that

[8] P. H. STELSON and F. K. MCGOWAN, *Phys. Rev.* **99**, 112, 616A (1955).

Vol. 15 1960

the 51·5 min activity was that of ^{98}Nb. This tentative assignment was confirmed by (n,p) reaction on ^{98}Mo. A sample of enriched ^{98}Mo was bombarded with D-T neutrons and the Nb fraction was chemically separated and examined. The resultant Nb activity displayed the 51·5 min half-life and the characteristic γ-spectrum of the Nb of fission origin.

The γ-spectrum of ^{98}Nb, after correction for the contribution of ^{97}Nb, is shown in Figs. 2 and 3. No subtraction was made for the ^{96}Nb γ-spectrum, since it represented

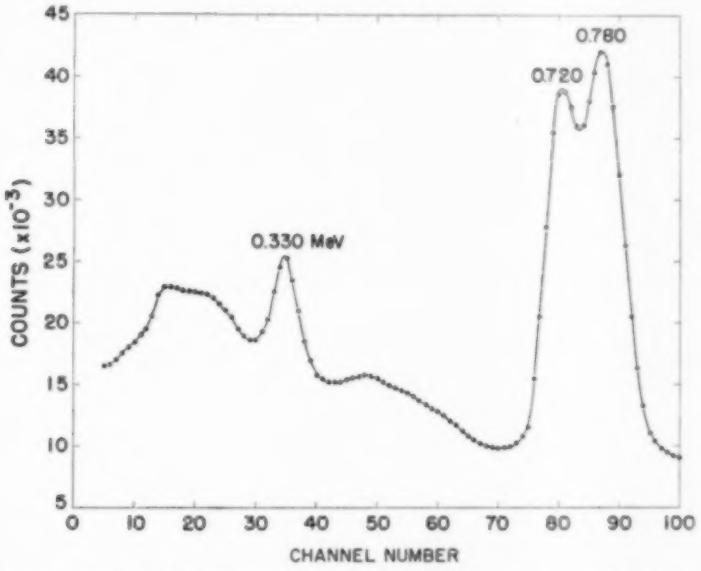

FIG. 2.—Scintillation γ-spectrum (low-energy region) of 51·5 min ^{98}Nb, measured with 3 in. × 3 in. NaI(Tl) crystal. The ^{97}Nb γ-spectrum has been subtracted out. Source distance: 1·4 cm.

$\lesssim$0·5 per cent of the disintegrations at the time measurements were made. In Fig. 3, a large part but not all of the 1·52 MeV photopeak is due to coincidence summing of the strong 0·720 MeV photo events. γ-Ray energies, relative intensities, β-groups, and coincidence data for ^{98}Nb are presented in Table 1.

The β-scintillation measurements indicated a complex spectrum with a maximum energy of 3·1 $\pm$ 0·2 MeV. A Fermi-Curie plot of the high-energy protion of the spectrum, together with plots of ^{32}P, ^{90}Y, ^{106}Ru–^{106}Rh and ^{144}Ce–^{144}Pr standards for purposes of comparison, are shown in Fig. 4.

(b) *Coincidence measurements on* ^{98}Nb. When the γ-spectrum is gated by the 0·780 MeV photopeak the 0·330, 0·720 and 1·16 MeV photopeaks are observed to be in coincidence, as shown in Fig. 5. Although not shown, the higher energy γ-rays tabulated in Table 1 were also observed to be in coincidence with the 0·780 MeV photopeak. The γ-spectrum was also gated by the 0·330, 0·720, 1·16, 1·68, 1·88 and 1·93 MeV photopeaks and the results are tabulated in Table 1.

When the γ-spectrum is gated by the 2·8–3·1 MeV portion of the 3·1 MeV β-spectrum, only the 0·720 and 0·780 MeV γ-rays are observed to be in coincidence, as shown in Fig. 6. Since the 0·720 and 0·780 MeV γ-rays are in cascade, and since

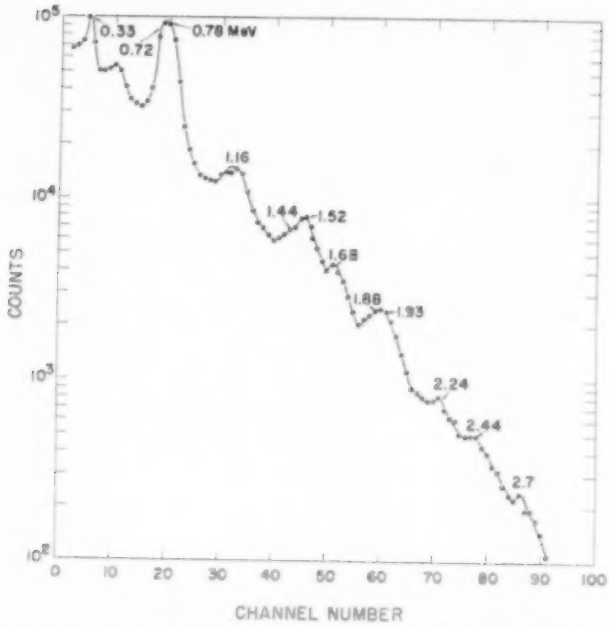

FIG. 3.—Scintillation γ-spectrum (high-energy region) of 51·5 min ^{95}Nb, measured with 3 in. × 3 in. NaI(Tl) crystal. The ^{97}Nb γ-spectrum has been subtracted out. Source distance: 1·4 cm.

TABLE 1.—SUMMARY OF ^{95}Nb DATA

E_γ(MeV)	Relative intensity	In coincidence with
0·330 ± 0·005	9 ± 3	0·720, 0·780
0·720 ± 0·005	75 ± 10	0·330, 0·780, 1·16, 1·44, 1·52, 1·68
0·780 ± 0·005	100	0·330, 0·720, 1·16, 1·44, 1·52, 1·68, 1·88, 1·93
1·16 ± 0·01	30 ± 5	0·720, 0·780
1·44 ± 0·02	10 ± 4	
1·52 ± 0·02	4 ± 2	
1·68 ± 0·02	10 ± 3	0·720, 0·780
1·88 ± 0·02	4 ± 2	0·780
1·93 ± 0·02	8 ± 3	0·780
2·24 ± 0·04		
2·44 ± 0·04		
2·7 ± 0·1		
E_β(MeV)	In coincidence with	
3·1 ± 0·2 (weak)	0·720 and 0·780 MeV γ-rays	
$t_{1/2}$ = 51·5 ± 1·0 min	Q_β = 4·6 ± 0·2 MeV	

they occur in equal intensities in the spectrum gated by the high-energy β-rays, Q_β is assumed to be the sum of these two γ-ray energies and the 3·1 MeV end-point of the β-spectrum, or 4·6 ± 0·2 MeV.

Vol. 15 1960

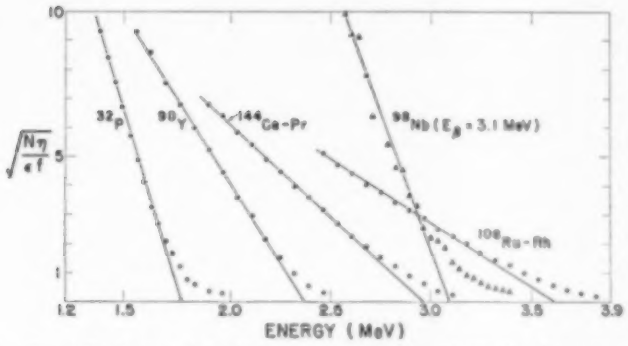

FIG. 4.—Fermi-Curie plot of the high energy end of the scintillation β-spectra of 51·5 min ^{99}Nb and of standards.

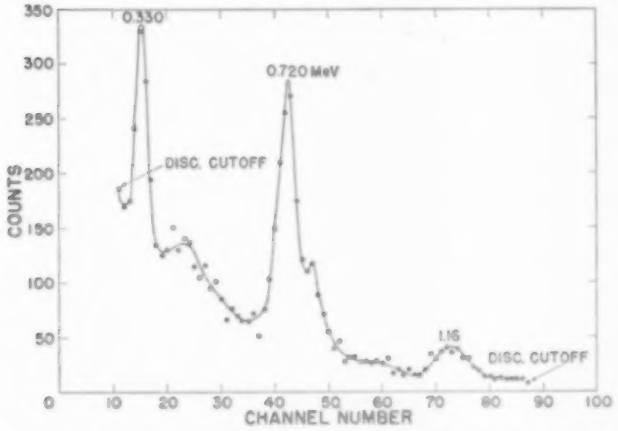

FIG. 5.—Scintillation γ-spectrum of 51·5 min ^{99}Nb gated by 0·780 MeV photo-peak. Spectrum measured with 1½ in. × 1½ in. NaI (Tl) crystal.

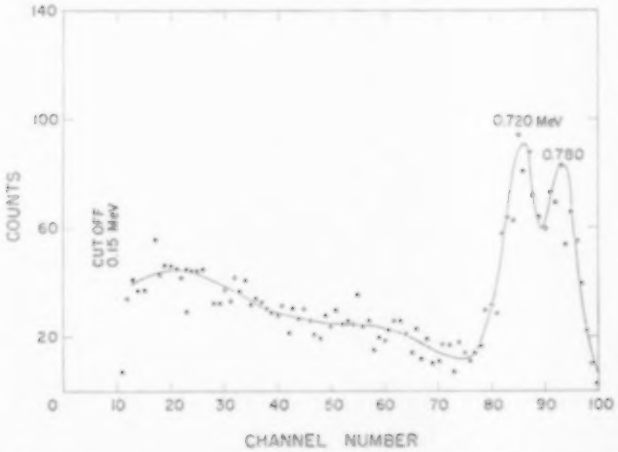

FIG. 6.—Scintillation γ-spectrum of 51·5 min ^{99}Nb gated by 2·8–3·1 MeV portion of β-spectrum. γ-spectrum was measured with 3 in. × 3 in. NaI (Tl) crystal. Detectors were placed at 90°.

(c) *Fission yield of* ^{98}Nb. A crude measurement of the relative fission yields of ^{98}Nb and ^{97}Nb by comparison of the 0·66 and 0·780 MeV photopeaks in Nb samples rapidly separated from Zr indicated the yield of ^{98}Nb was about four times that of ^{97}Nb. When Nb was milked from Zr at early times, ^{97}Nb grew from Zr, but ^{98}Nb was not observed to grow from the Zr. These measurements are in fair agreement with the careful work done by TROUTNER[4], who reported an independent fission yield of 0·0017 per cent for ^{97}Nb and a total yield of 0·011 per cent for ^{98}Nb. Since the fission yield of ^{98}Mo

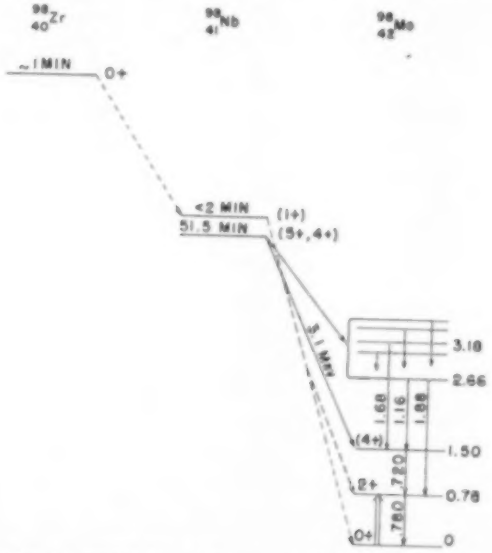

FIG. 7.—Partial decay scheme proposed for ^{98}Zr–^{98}Nb.

has been measured to be 5·8 per cent by STEINBERG and GLENDENIN[9], it appears that >99 per cent of the mass 98 β-decay chain by-passes the 51·5 min ^{98}Nb, presumably via a low-spin isomer of ^{98}Nb.

(d) *Partial* ^{98}Nb *decay scheme.* As shown in Table 1, the 0·780 MeV γ-ray is the most abundant, both in the singles and in the coincidence spectra. From Coulomb excitation work,[8] this γ-ray is known to represent the transition from the first 2+ level to the 0+ ^{98}Mo ground state. The second most prominent γ-ray, 0·720 MeV, is in coincidence with the 0·780 MeV γ-ray and is presumed to represent the transition from the first 4+ level at 1·50 MeV to the 2+ level at 0·780 MeV. The 1·16 and 1·68 MeV γ-rays are in coincidence with both the 0·720 and 0·780 MeV γ-rays, but not with each other. These observations indicate levels at 2·66 and 3·18 MeV as shown in the decay scheme (Fig. 7). A small fraction of the 51·5 min ^{98}Nb β-transitions proceed to the level at 1·50 MeV. The fact that the 0·720 and 0·780 MeV γ-rays are in coincidence, in equal intensity, with the high energy portion of the 3·1 MeV β-spectrum, indicates that the 2+ level at 0·780 of ^{98}Mo is not directly fed to any appreciable extent. These conclusions suggest a spin of four, five or six for 51·5 min ^{98}Nb.

For the ^{98}Nb nucleus, which contains forty-one protons and fifty-seven neutrons,

[9] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 3. United Nations (1956).

Vol. 15 1960

the low-lying proton states are $p_{\frac{1}{2}}$ and $g_{\frac{9}{2}}$ and the low-lying nuetron states are $d_{\frac{5}{2}}$, $g_{\frac{7}{2}}$ and possibly $s_{\frac{1}{2}}$. Of the two eligible proton states, the $g_{\frac{9}{2}}$ state may be expected to be the lower. It lies 0·23 MeV below the $p_{\frac{1}{2}}$ state at ^{95}Nb and 0·75 MeV below the $p_{\frac{1}{2}}$ state at ^{97}Nb. Coupling of the $g_{\frac{9}{2}}$ proton with the three neutron groups according to NORDHEIM's rule[10] gives $\leqslant 7+$, $1+$, and $\leqslant 5+$, respectively. Of these possibilities, the experimental evidence favours either $4+$ or $5+$ for 51·5 min ^{89}Nb. The evidence that most of the mass 98 β-decay chain proceeds through a short-lived isomer of ^{98}Nb

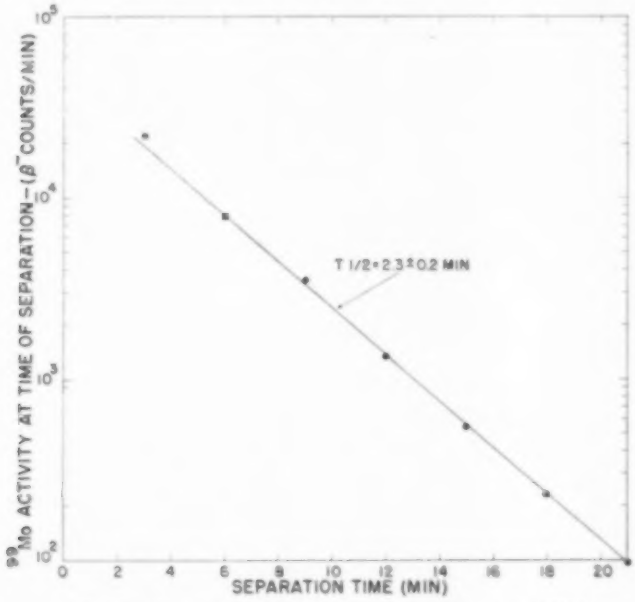

FIG. 8.—Decay curve of ^{99}Nb by periodic separation of ^{99}Mo.

can be interpreted by assignment of the latter as a $1+$ state. The hypothetical $1+$ level is sketched in Fig. 7, although its position relative to the high-spin isomeric level is not known.

2. ^{99}Nb

The half-life of ^{99}Nb was measured by milking Mo from fission product Nb as discussed in *Chemical procedures* (3). The plot of the ^{99}Mo β-activity extrapolated to time of separation is shown in Fig. 8. The half-life of ^{99}Nb from the curve is $2{\cdot}3 \pm 0{\cdot}2$ min.

Additional information on the short-lived Nb activity was obtained from several series of γ-scintillation spectra of Nb separated from fission products by *Chemical procedures* (1). The chemical separation was completed $\sim$12 min after end of irradiation and spectrum measurements were begun $<$2 min later. Representative spectra are shown in Figs. 9 and 10. In Fig. 9, only the 0·100- and 0·260 MeV photopeaks decay with a 2·5 min half-life, while the others decay with $\sim$3·0 min half-life. The 0·100 MeV photopeak may correspond to the 0·098 MeV γ-ray from a metastable

[10] L. A. NORDHEIM, *Rev. Mod. Phys.* **23**, 322 (1951).

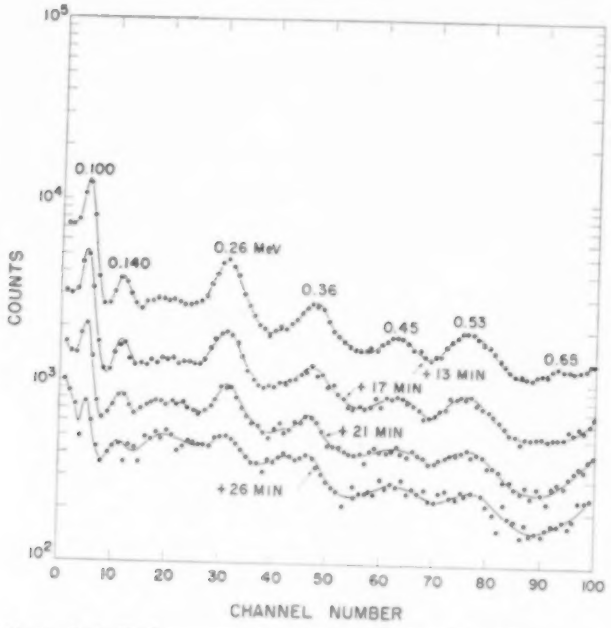

FIG. 9.—Series of scintillation γ-spectra (low-energy region) of Nb rapidly separated from fission products, measured with 2 in. × 2 in. NaI(Tl) crystal. Count length: 2 min.

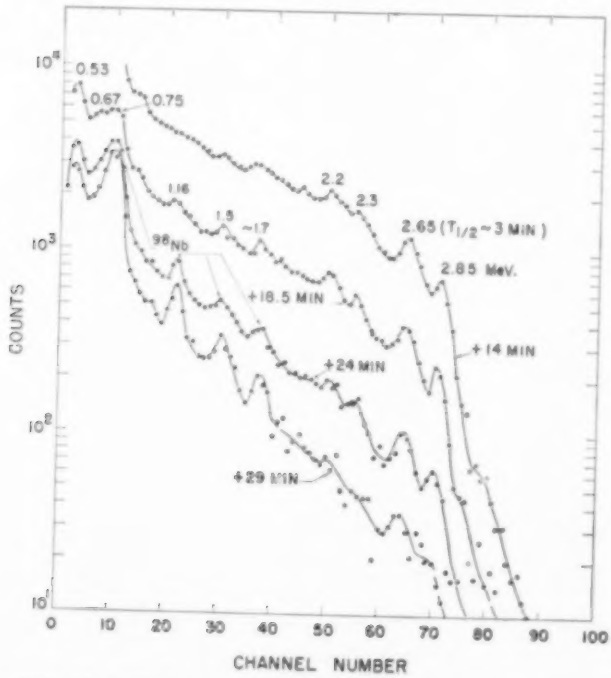

FIG. 10.—Series of scintillation γ-spectra (high-energy region) of Nb rapidly separated from fission products, measured with 2 in. × 2 in. NaI(Tl) crystal. Count length: 2 min.

Vol. 15 1960

level of ^{99}Mo observed by VEGORS and AXEL[11], who produced it by the ^{100}Mo(γ,n) reaction.

The 2·3 ± 0·2 min half-life obtained by milking ^{99}Mo was averaged with the 2·5 ± 0·2 min decay period of the 0·100 MeV photopeak to give a half-life of 2·4 ± 0·3 min for ^{99}Nb. This value is in good agreement with the 2·5 min period measured by DUFFIELD *et al.*[2]

TABLE 2.—SUMMARY OF ^{99}Nb, ^{100}Nb, ^{101}Nb, ^{98}Zr AND ^{99}Zr DATA

Nuclide	Half-life	$E\gamma$ (MeV)	Relative intensity	In coincidence with
^{99}Nb	2·4 ± 0·3 min	0·100 ± 0·002	1	
		0·260 ± 0·005	1	
^{100}Nb	3·0 ± 0·3 min	0·140 ± 0·005	10 ± 3	
		0·360 ± 0·010	55 ± 10	
		0·450 ± 0·010	40 ± 10	
		0·530 ± 0·010	100	0·140, 0·360, 0·450, 0·530
		0·650 ± 0·010		
		2·2 ± 0·1		
		2·3 ± 0·1		
		2·65 ± 0·05		
		2·85 ± 0·05		
^{101}Nb	1·0 ± 0·2 min			
^{98}Zr	~ 1 min			
^{99}Zr	35 ± 5 sec			

3. ^{100}Nb

The photopeaks of the complex Nb γ-spectrum which decayed with a 3 min period appeared to belong to another isotope of Nb as yet unreported. The similarity in energy of the most intense photopeak at 0·530 MeV to the position of the first excited (2+) state of ^{100}Mo as measured by Coulomb excitation[8,12] suggested the assignment of the 3·0 ± 0·3 min period to ^{100}Nb. γ-ray energies, relative intensities and coincidence data associated with the 3·0 min activity are given in Table 2.

γ–γ Coincidence measurements showed that when the Nb γ-spectrum was gated by the 0·530 MeV photopeak, the 0·14, 0·36, 0·45 and 0·53 MeV γ-rays were observed as shown in Fig. 11. Inspection of this plot reveals two significant features: (1) the 0·260 MeV γ-ray assigned to ^{99}Nb is absent (the 0·100 MeV peak lies below the discriminator cut-off); (2) the 0·530 MeV photopeak appears to be in coincidence with itself, indicating that it is actually a doublet.

An attempt to verify the above mass assignment by bombardment of enriched ^{100}Mo with D-T neutrons gave abundant ^{99}Mo (produced by the (n,2n) reaction) but gave no detectable amount of a 3 min Nb activity. With the assumption that the 3 min activity is correctly assigned, the experimental data yield an upper limit to the ^{100}Mo

[11] S. H. VEGORS, JR. and P. AXEL, *Phys. Rev.* **101**, 1067 (1956).
[12] G. M. TEMMER and N. P. HEYDENBURG, *Phys. Rev.* **104**, 967 (1956).

(n,p) cross-section of $\leqslant 0{\cdot}5$ mbarns at 14 MeV. This negative result is not necessarily inconsistent with the postulated mass assignment in view of the Q_β of ^{100}Nb and consequent unfavourable energy balance predicted for the (n,p) reaction.

4. ^{101}Nb

The half-life of ^{101}Nb was obtained by making successive separations of Mo from fission-product Nb as described in *Chemical procedures* (3). The decay of the 0·30 MeV

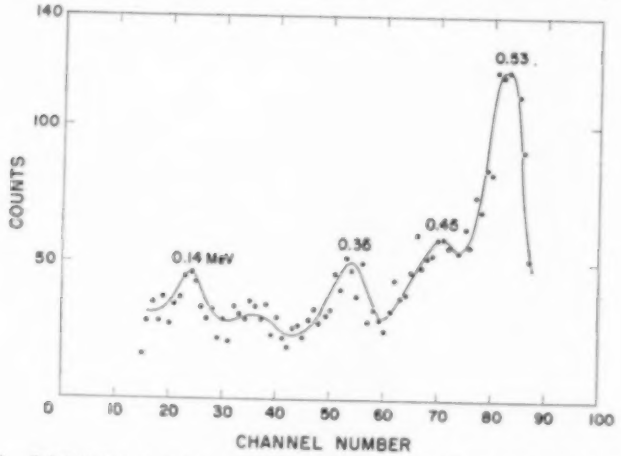

FIG. 11.—Scintillation γ-spectrum of Nb rapidly separated from fission products, gated by 0·530 MeV photopeak. Spectrum measured with 2 in. × 2 in. NaI(Tl) crystal.

photopeak of ^{101}Tc which had grown in from ^{101}Mo was followed for each separation. Corrections were made for growth and decay, time of separation and chemical yields. The ^{101}Mo activities so derived, plotted in Fig. 12, gave a ^{101}Nb half-life of $1{\cdot}0 \pm 0{\cdot}2$ min.

5. ^{98}Zr

β- and γ-decay measurements of fission product Zr isolated by the longer TTA extraction method described in *Chemical procedures* (2) showed no activity attributable to a Zr nuclide with a half-life between 2 min and 17 hr. Since on the basis of β-decay systematics, ^{98}Zr may be predicted to have a $Q_\beta \sim 2$ MeV, the 2 min upper limit on its half-life corresponds to a $\log ft \leqslant 4{\cdot}6$ for β-decay to ^{98}Nb. With the assumption of a 0+ level assignment for ^{98}Zr, this low $\log ft$ value indicates decay to a 1+ ground-state or near ground-state level in ^{98}Nb. Furthermore, the fission-yield data for 51·5 min ^{98}Nb and stable ^{98}Mo show that virtually all ^{98}Zr must decay to another isomer of ^{98}Nb, presumably of low spin. An upper limit for its half-life could be deduced from the β-decay data of rapidly separated Nb. From the absence of β-decay components of the necessary intensity in the time range covered, it was deduced that the half-life of the isomer is $\leqslant 2$ min.

With the assumption that the β-decay of ^{98}Zr is followed by the rapid decay of a Nb daughter by a high energy β-transition ($\sim 4{\cdot}6$ MeV), a search was made for a short period in the decay of energetic β-radiation from rapidly separated fission-product Zr.

Vol. 15 1960

The Zr was separated from fission products by the faster TTA method described in *Chemical procedures* (2), and the 3 ml of TTA solution containing the Zr activity was β-counted directly in a plastic cup through 860 mg cm^{-2} Al absorber. The early portion of the Zr decay is plotted in Fig. 13. Since radiochemical analysis of the TTA solution 19 hr after end of the irradiation revealed a relatively large amount of ^{97}Zr and traces of ^{99}Mo and ^{132}Te, the ~15 min and ~1 hr activities deduced from later

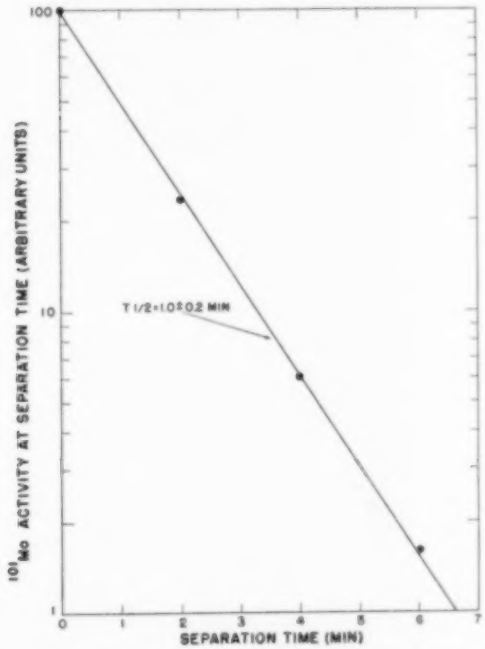

FIG. 12.—Decay curve of ^{101}Nb by periodic separation of ^{101}Mo.

counts are probably due to Mo, Te and possibly Ce contaminants. If the contaminants are considered on an atom per cent basis, they can amount to $\leqslant$10 per cent of the strong 1 min component. On the basis of these observations the 1 min activity is assigned to an isotope of Zr, possibly ^{98}Zr.

6. ^{99}Zr

An approximate measurement of the half-life of ^{99}Zr was obtained by milking of ^{99}Nb–^{99}Mo from fission-product Zr as described in *Chemical procedures* (4). The ^{99}Mo β-activity from each separation is plotted in Fig. 14. The ^{99}Zr half-life deduced in this manner is 35 $\pm$ 5 sec. This value agrees with the 30 sec period reported for ^{99}Zr by PAPPAS and THOMPSON[3].

7. *Search for isomerism in* ^{96}Nb

Published information on the decay of 23 hr ^{96}Nb [13,14] indicates that its spin is $\geqslant$5. This spin can be accounted for by coupling of a $g_{\frac{9}{2}}$ proton with a $d_{\frac{1}{2}}$ neutron,

[13] P. PREISWERK and P. STAHELIN, *Helv. Phys. Acta* **24**, 300 (1951).
[14] D. R. JONES, S. C. FULTZ and M. L. POOL, *Phys. Rev.* **86**, 654 A (1952).

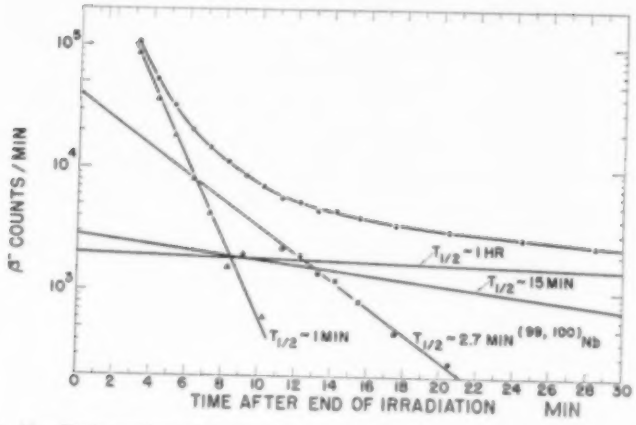

FIG. 13.—Early portion of the decay curve of Zr rapidly separated from fission products.

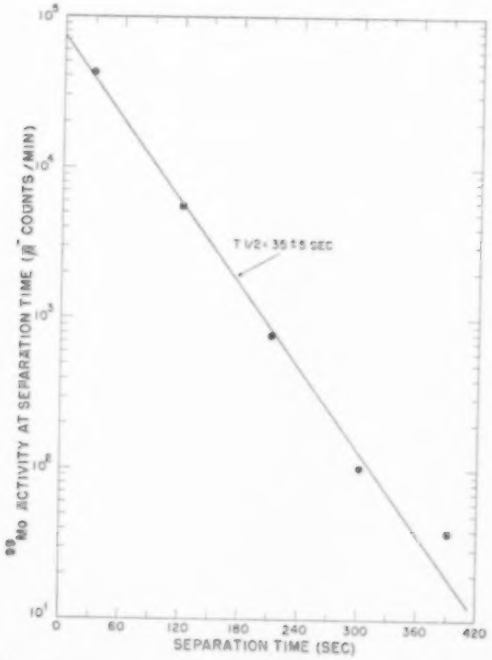

FIG. 14.—Decay curve of ^{99}Zr by periodic separation of ^{99}Nb–^{99}Mo.

with a resultant spin and parity of $\leqslant 7+$. There also exists the possibility of an isomeric state with spin $1+$ due to coupling of the $g_{\frac{9}{2}}$ proton with a $g_{\frac{7}{2}}$ neutron. With the assumption of $Q_\beta \sim 3{\cdot}1$ MeV, such an isomer would be expected to have a β-half-life of $\sim$15 sec.

To investigate this possibility, normal Zr metal was irradiated with protons ranging in energy from 3·0 to 5·5 MeV to produce ^{96}Nb by the (p,n) reaction on ^{96}Zr. Twenty-three hour ^{96}Nb and 6·6 min ^{94m}Nb were produced in high yield but no other activity

Vol. 15 1960

in the half-life range 5 sec to 10 hr which could be attributed to an isomer of ^{96}Nb was observed by β- and γ-scintillation counting. The $1+$ level possibly lies quite high above the $\geqslant 5$ ground state and perhaps a level of intermediate spin ($3-$ or $4-$) lies between them. Such an intermediate level with reasonable energy spacings could shorten the isomeric transition half-life to less than 5 sec.

Acknowledgements—The authors wish to express their appreciation to M. M. THORPE, J. MONTOYA, and JANE HEYDORN for the thermal neutron irradiations and to R. W. DAVIS for the Cockcroft–Walton irradiations. We are indebted to Drs. J. D. KNIGHT and B. J. DROPESKY for their helpful discussions and suggestions and to Dr. G. A. COWAN for his encouragement throughout this work.

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A METHOD FOR THE ENRICHMENT OF RADIOISOTOPES PRODUCED BY (γ,n)*

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(*Received* 14 *September* 1959)

Abstract—A method has been developed to enrich radioisotopes produced by (γ,n) which is based on catching the recoils from the finely divided material in a solidified phase of 20 per cent by weight gelatine in water. The method has been applied to Ti and Cu, giving enrichment factors of 100 and 4·0 respectively.

THERE have been several cases in which radioisotopes produced by (γ, n) have been successfully enriched by catching the recoiling nuclues in another phase. MORINAGA and ZAFFARANO[1] have enriched ^{11}C produced from natural carbon in Aquadag solution. PAULY and SUE[2] have enriched ^{30}P by irradiating a suspension of red phophorous in tetraline. They have succeeded also[3] in enriching ^{62}Cu by irradiating a finely divided mixture of $CuSO_4$ and $CaCO_3$.

In the present work we describe a method to enrich radioisotopes produced by (γ,n) in which the catching phase is water.

EXPERIMENTAL PROCEDURE AND RESULTS

The samples for irradiation were prepared by melting 10 g of gelatine in 40 g of water at 60°C and keeping it at this temperature. Twenty grammes of finely divided TiO_2 were warmed up to 60°C and thoroughly mixed with the water phase. The suspension was transferred to a mould and allowed to become solid. It stayed solid at room temperature. The solidified suspension was irradiated for 2 hr with γ-rays from the betatron at the University of São Paulo. The γ-rays had a maximum energy of 21 MeV. The samples were flown to our laboratory in Rio de Janeiro, where they were melted in 100 ml of 1 N HCl. The TiO_2 was filtered. A small amount of Ti was dissolved and remained in the filtrate. This Ti was precipitated with NH_4OH and filtered. The TiO_2 and the $Ti(OH)_4$ were placed inside plastic boxes and counted with identical geometry with NaI(Tl) scintillation spectrometer set to count the peak of 511 keV annihilation γ-rays from the positrons of ^{45}Ti. It was found that 10 per cent of the total activity was in the hydroxide and that its weight as TiO_2 was 20 mg. This gives an enrichment factor of 100.

A similar experiment was carried out by substituting the 20 g of TiO_2 by 20 g of CuO. The irradiated sample was melted in 100 ml of boiling 0·01 N HCl. The CuO was centrifuged to coagulate it and then filtered. A small amount of Cu was dissolved and remained in the filtrate as Cu^{2+}. It was reduced at 100°C with Na_2SO_3 and

* This work was done in part under the auspices of the Comissao Nacional de Energia Nuclear and the Conselho Nacional de Pesquisas of Brazil.

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[1] H. MORINAGA and D. ZAFFARANO, *Phys. Rev.* **93**, 1422 (1954).
[2] J. PAULY and P. SUE, *C. R. Acad. Sci., Paris* **240**, 2226 (1955).
[3] J. PAULY and P. SUE, *C. R. Acad. Sci., Paris* **241**, 197 (1955).

Vol. 15 1960

precipitated as CuSCN with NaSCN, cooled in an ice-bath and filtered with vacuum in a filter paper. The CuO and the CuSCN were placed inside plastic boxes and counted with the scintillation spectrometer set again to count the peak of the annihilation γ-rays from the positrons of ^{64}Cu. It was found that 0·29 per cent of the total activity was in the CuSCN and its weight expressed as CuO was 46·0 mg. This gives an enrichment factor of 4·0.

The size of the particles was estimated from the filtration properties of the suspended particles through several kinds of filter paper. They were of the order of a few microns. The particles of TiO_2 were much smaller than the particles of CuO and this accounts for the larger yield of the former.

The recoil energy of the radioisotope is $E_n/(A-1)$, where E_n is the energy of the emitted neutron and A is the mass number of the target. The energy of the emitted neutron will be determined by the evaporation theory and will be roughly the same for Ti and Cu, so one does not expect marked differences in the recoil energies.

The chemical procedure was chosen so that there would be a tendency of the surface to dissolve rather than a tendency of the dissolved cations to precipitate on the surface. Aside from that, we did not study any influence of heterogeneous exchange.

It seems to us that the method can be applied to any element if it forms a compound that is insoluble in water and if this compound can be prepared as a fine powder. The enrichment factor can possibly be made much greater by improving our technique.

Acknowledgement—We are greatly indebted to Prof. J. GOLDEMBERG, in charge of the Laboratorio do Betatron in São Paulo, for making the irradiations without which this work would not have been possible.

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RADIOCHEMICAL ANALYSIS OF INDIVIDUAL FALL-OUT PARTICLES

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(*Received* 19 *October* 1959)

Abstract—Quantitative measurements were made of the radioactivity of individual fall-out particles from a nuclear detonation at the Eniwetok Proving Grounds. These measurements were possible since individual particles which represented approximately 10^{19} or more fissions were obtained. Although several types of particles were observed, the data were generally resolved as being derived from two major particle classes depending upon whether the coral had undergone an obvious physical alteration such as melting.

A number of individual particles were radiochemically analysed for the nuclides ^{99}Mo, ^{140}Ba–^{140}La, ^{89}Sr and ^{239}Np. The data obtained, together with γ-spectral and decay measurements, indicate that fractionation of radionuclides was prominent in the fall-out particles. Measured R values for ^{140}Ba and ^{89}Sr based on ^{99}Mo were over an order of magnitude lower in the altered particles than in the more normal appearing or unaltered particles. The fissions/gramme values of altered particles averaged 100 times that of unaltered particles. γ-Decay curves of the two classes of particles taken from H + 50 to H + 10,000 hr showed marked dissimilarities.

Vol.
15
1960

THE radiochemical compositions of fall-out from several nuclear weapons tests have been studied by many investigators.[1] With few exceptions all such studies were conducted with large fall-out collections, i.e. with fall-out collections each of which was composed of many individual particles. Although individual particles as separate entities have been examined, very few investigations of the radiochemical compositions of individual fall-out particles have been reported. Moreover, the radioactivity data obtained in these particle studies were of a relative nature.

Individual particles have been examined with spectrographic microscopes, by combined thin sectioning and photomicrography, through emission spectrograph chemical tests, and by X-ray diffraction patterns, using samples from several nuclear test series. While the chemical and physical states of single particles were effectively described, no information was obtained concerning the absolute amount of radioactivity or the amounts of specific radionuclides present. Some information concerning activity was obtained through the study of autoradiographs which described the location of activity on individual particles.[2] In some cases, radiochemical analyses were performed on crudely sized particles but there was no attempt to separate active from inactive particles.

Several investigators have performed γ-spectral analysis of gross bomb debris and/or individual, active particles. These studies have yielded much information

[1] With few exceptions, reports of such studies have appeared in the classified literature. An unclassified version of the present report has been published as a USNRDL Technical report and contains pertinent references to the classified literature. Examples of the work carried out in this field which have been reported in the open literature include: S. GLASSTONE (Editor), *The Effects of Nuclear Weapons*. U.S. Govt. Printing Office, Washington (1957); K. KIMURA, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, P/1058, pp. 196–209. United Nations (1956).

[2] C. E. ADAMS, N. H. FARLOW and W. R. SCHELL, USNRDL-TR-209 (1958); *Geochim. Cosmochim. Acta* **18**, 426 (1960).

about the spectral characteristics of radiation from fall-out particles and some (relative) information concerning their radiochemical composition. Gross γ-ray spectral data, however, are not particularly amenable to absolute or even relative determination of the radionuclide composition of active particles, particularly for large numbers of samples.

The considerable amount of radiochemical work on total mixtures and the work on physical and γ-spectral measurements of individual particles has been useful to define fall-out hazards and to develop theories for prediction of such hazards. Without elaboration, however, it may be stated that the general application of such data to hazard definition and prediction and to such problems as fall-out formation theory, radiological decontamination, fractionation of radioactive nuclides, etc. has been restricted by a lack of knowledge concerning the nuclide composition of individual particles. The acquisition of such knowledge by radiochemical analysis of single fall-out particles is a logical extension of both past and present studies on gross samples of radioactive fall-out. Such analyses have the advantage of starting with simple systems from which theoretical deductions may be derived for more complex systems.

Since little quantitative information was available concerning levels of radioactivity or of specific nuclides associated with single particles of fall-out the primary purpose of the present work was to explore the feasibility of such analyses. For the purpose of this investigation feasibility was defined as the ability to quantitatively assess individual particle radioactivity. It was estimated that individual particles containing radioactivity from approximately 10^{10} fissions would be required for such assessment. It was further intended that, if, indeed, such analyses were feasible sufficient data would be obtained to establish amounts of several nuclides and to search for differences (i.e. fractionation) in radionuclide composition between individual particles.

Measurements were carried out on particles from a nuclear detonation of Operation REDWING. The detonation took place at Bikini Atoll in the Spring of 1956. Individual particles were examined to determine total radioactivity and to estimate the number of fission events leading to such radioactivity. Analyses were made of the ^{89}Sr, ^{99}Mo, ^{140}Ba and ^{239}Np content and of the weight of separate particles. γ-Ray spectra and rates of decay of particles were obtained.

PROCEDURES

This section considers three topics. These are counting instrumentation, calibrations and measurements.

Description of counting instrumentation

Several types of counting instruments were used in these experiments. Brief descriptions of these instruments are given below.

(a) *γ-Well counter.* The γ-well counter (termed the "WC") consists of a cylindrical well-type NaI(Tl) crystal, $1\frac{1}{2}$ in. diameter by 2 in. long, coupled to a 6292 DuMont phototube which in turn is connected to a preamplifier and scaling circuit. The counting efficiency of the system increases with decreasing energy of the γ-ray under assay (except at very low energies).

(b) *High pressure γ-ionization chamber.* The high pressure γ-ionization chamber (termed the "GIC") is similar in design and operation to the chamber described by JONES and OVERMAN[3]. This instrument consists essentially of a large steel chamber containing argon gas at 600 psig. All data

[3] J. W. JONES and R. T. OVERMAN, Oak Ridge National Laboratory, AECD-2367 (1948).

procured on this instrument were normalized relative to a 100 μg radium standard response of 560×10^{-9} mA of ionization current. The counting efficiency of this instrument is a function of γ-ray energy and increases with increasing γ-energy.[4]

(c) *Proportional β-counters.* The scaling portions of these counters are of conventional nature. Detectors consist of semi-cylindrical longitudinal chambers containing 1 mil tungsten wires. The counter gas is 90 per cent argon and 10 per cent carbon dioxide by volume. The gas flows continuously above a 1 mg/cm^2 aluminized Mylar window. Solid counting samples are contained in filter paper disks mounted on brass planchets which are indexed to a reproducible position in aluminium holders.

(d) *Single channel γ-pulse height analyser.* The unit consists of a $1\frac{1}{2} \times 1$ in. NaI detector, linear amplifier, analyser, step scanner and digital recorder. The small crystal employed with the analyser is useful for scanning the low-energy portion of the fission product spectrum for photopeaks from ^{239}Np and ^{99}Tc.

Calibrations

Prior to receipt of the fall-out samples a number of preliminary experiments were made using enriched uranium (93·2% ^{235}U) samples irradiated in a high neutron flux for periods less than 30 min. The purpose of these experiments was to investigate the accuracy and reproducibility of individual measurements which were contemplated, establish a procedure for manipulations of the fall-out samples, define minimum acceptable activity levels, inter-calibrate counting instruments and provide "normal" decay curves for radioactive mixtures produced by thermal neutron fission of ^{235}U.

Measurement

Three primary types of analytical determinations were carried out. These were radioactivity measurements, radiochemical analyses and weight determinations. The specific determinations and the reasons for the determinations are described below.

(a) *Radioactivity measurements.* Most of the activity determinations consisted of measurements of γ-radiation with either (or both) the high pressure γ-ionization chamber (GIC) or the γ-well counter (WC). The values obtained on these instruments were used for primary assay purposes, to establish rates of decay and to compare the γ-activities of different particles by calculation of three activity ratios. These ratios were: (a) well counts per minute per milliampere (WC c.p.m./mA); well counts per minute per 10^4 fissions (WC c.p.m./10^4f); and milliamperes per 10^4 fissions (mA/10^4f).

Both the numerator and the denominator values of the ratio WC c.p.m./mA were obtained with instruments whose detection efficiences varied with γ-energy. As noted above, the efficiency of the well counter decreased with increasing γ-energy, whereas the efficiency of the ionization chamber increased with increasing γ-energy. Consequently, the ratios, WC c.p.m./mA, for single particles (at a given time) reflect differences in the radionuclide compositions of the particles. Thus, the WC c.p.m./mA ratios obtained at the same time for two particles may be compared to investigate gross differences in radionuclide compositions of the two particles. In addition, the WC c.p.m./mA ratios of a large number of samples have the advantage of being easily measured without recourse to fission determinations.

Computations of the ratios WC c.p.m./10^4f and mA/10^4f were carried out for the following reasons. In the examination of radioactive fall-out it is common practice to present analytical results in terms of fission events which the sample radioactivity (or sample radionuclide composition) represents, that is, the number of fission events which result in the sample radioactivity (or sample radionuclide composition). The value for number of fission events is determined by radiochemical analysis for ^{99}Mo as described later in this report. Using fissions (i.e. 10^4f*) as the denominators in the ratios has the advantage of providing a single comparison base which, in itself, is not dependent upon time of analysis and which does not change with time. Moreover, each ratio reflects radionuclide composition. As such, it is possible to compare either the WC c.p.m. or mA per fission ratios of a number of particles to distinguish differences in radionuclide compositions of the particles. In

* The unit "10^4 fissions" is widely used as a convenient computational base at this Laboratory for radiochemical and radioactivity measurements.[5,6]

[4] C. F. MILLER, USNRDL-TR-155 (1957).
[5] C. F. MILLER, USNRDL-TR-187 (1957).
[6] R. C. BOLLES and N. E. BALLOU, USNRDL-456 (1956).

Vol. 15 1960

addition, the ratios may be used to compute total fissions for particles which have not been subjected to radiochemical analysis but have been assayed on the well counter and ionization chamber.

Other radioactivity measurements were carried out with the single channel pulse height analyser and with the β-counter. The analyser was used to measure ^{99}Mo and ^{239}Np (as described below) and also to obtain γ-spectra which were employed in the interpretation of other measurements. The β-counter was used in the assay of individual separated fission products.

The times of all radioactivity measurements are given as time since detonation (TSD), frequently in terms of H + hours.

(b) *Radiochemical analyses.* A number of individual particles were dissolved and radiochemically analysed to investigate differences in radionuclide composition between the particles. The particles were placed in a small volumetric flask under a low power binocular microscope. The sample was then dissolved by application of various reagents. Most of the solid material (and activity) of a single particle dissolved in a few drops of 6 N HCl. The remaining solids usually consisted of small black particles which appeared to be carbonaceous and which were brought into solution by addition of one or two drops of 72% $HClO_4$ and warming.

Conventional radiochemical procedures were used in the analyses of ^{89}Sr, ^{140}Ba–^{140}La, and in some cases, ^{99}Mo.[7,8] Normally aliquots of a single solution of the dissolved sample were used. However, with low activity samples it was necessary to employ a sequential analysis of the entire sample solution. Some ^{99}Mo analyses were carried out by use of the single channel pulse-height analyser. The latter technique is based on analysis of the photopeak area of daughter ^{99m}Tc.[9] The agreement between the two methods was usually within 10 per cent when carried out on the same samples. Similar photopeak area analyses were used to determine amounts of ^{239}Np.

The radiochemical results were calculated in terms of ^{239}Np product to fission (p/f) ratios or R values. The former values were calculated directly from the numbers of atoms of the induced activity ^{239}Np, and the total fissions as calculated from the number of atoms of ^{99}Mo for each sample. The R values for ^{140}Ba and ^{89}Sr were defined in the usual manner by the ratio of atoms of the nuclide to the atoms of the reference nuclide, ^{99}Mo, as observed in the sample divided by the same ratio for thermal neutron fission of ^{235}U. From this definition it is apparent that R values from fall-out samples indicate the combined effects of fractionation and variations in fission yield. Although lower than thermal fission yields for ^{89}Sr and ^{140}Ba were expected for fast neutron fission,[10,11,12] the deviation was considered to be not greater than 20 per cent. For ^{99}Mo the deviation was probably less and therefore all fission calculations were based on a thermal fission yield for ^{99}Mo of 6·1 per cent. These same considerations together with experimental uncertainties generally lead to observed R values of 1·0 ± 0·5 and which are considered "normal" within these limits.

(c) *Weight measurements.* Selected particles were weighed. Most of these measurements were carried out on a Ainsworth microbalance. The data obtained were used to compute the values for the number of fissions per unit weight of fall-out particles. Such values were compared to similar values obtained with gross collections of fall-out materials.

SAMPLES

The numbers of samples received, their manner of collection and initial assay

A total of 300 particles were received from the laboratory of a manned ship, which was positioned to receive fall-out from the event. The particles were obtained from greased trays exposed sequentially during fall-out by a special collector arrangement. These trays were examined under a microscope in a shielded laboratory in the ship and randomly selected particles were removed with individual needles. A small amount of grease had been placed on the needle before the particle was removed; this insured adhesion of the particle. Prior to use, each needle was mounted in a cork, allowing the needle and particle to be inserted in a small glass phial for shipment. After receipt at San Francisco, each particle was measured on the GIC and WC at approximately H + 72 hr; the most active

[7] C. D. Coryell and N. Sugarman (Editors), *Radiochemical Studies: The Fission Products*, NNES, Plutonium Project Record, Div IV, Vol. 9. McGraw-Hill, New York (1951).
[8] M. Lindner, UCRL-4377, 10 Aug. 1954.
[9] L. D. McIsaac, USNRDL-TR-72 (1956).
[10] G. P. Ford and J. S. Gilmore, LA-1997 (1956), CLASSIFIED.
[11] J. G. Cuninghame, *J. Inorg. Nucl. Chem.* **5**, 1 (1957).
[12] S. Katcoff, *Nucleonics* **16**, No. 4, 78 (1958).

samples assayed approximately 10^5 c.p.m. in the WC. Thirteen of the more active particles were selected for analyses. Most of these were dissolved; a few were retained intact for γ-spectral measurements and decay determinations.

Additional particles were obtained from two gross fall-out samples. These samples consisted of fall-out collected in a large tray on one of the islands of the Atoll (designated Island sample) and a sample removed from the deck of a platform on a barge which had been anchored in the lagoon. The latter sample was designated the Barge sample.

After return to San Francisco, twenty-one particles were removed at random from the Island sample with a small spatula, placed on glass slides for microscopic observation and were later transferred to individual glass tubes for radioactivity assay. Following this, each particle was subjected to analyses.

Particles were removed from the Barge sample before and after sieving of the entire sample. Eighteen individual particles were removed before sieving.* These were designated 165W through 182. Of these, two (170 and 177) were analysed radiochemically. The remaining sixteen particles were γ-counted and weighed. The entire sample was then sieved, and each size fraction weighed, measured in the GIC and placed in separate dishes. Under a microscope individual particles were scooped from large numbers of particles on each dish. Each particle was held under the microscope, typed and was placed in a separate phial for assay in the WC. Almost 650 particles were assayed. After this, a number of particles typed and designated *WI* (see below) from the 500–1000 μ sieve fraction were combined and treated as one sample. The same procedure was followed with a number of particles typed *YS* and also a number typed *WS*.

Selection of individual particles

In all cases selections of individual particles from large groups of particles were made in a random manner except for eighteen particles from the Barge sample as described earlier. Among a number of operators the following particle colours and particle shapes were observed by microscopic examination (abbreviating symbols used are listed):

Colour		Shape	
Yellow	*Y*	Spherical	*S*
White	*W*	Flaky	*F*
Gray	*G*	Irregular	*I*
Colourless	*C*	Angular	*A*

Some particles which were comparatively light in colour were observed; this decrease in colour intensity was noted by addition of the letter *L* to the colour designator. More detailed descriptions of particle classification parameters have been reported elsewhere.[12,13]

It was generally agreed that the spherical and flaky particles represented an obvious physical alteration of the normal appearing (angular or irregular) coral particles. In some instances, it was difficult to type individual particles by colour. However, particles which had obviously been physically altered in some manner were usually easily distinguished. As a consequence, the information obtained in this investigation has been considered to have been derived from two general classes of particles—altered and unaltered. The altered were defined as particles possessing spherical shapes (presumably melted) or particles which were flaky; unaltered particles were defined to consist of irregular or angular particles. ADAMS has stated[14] that almost all particles of both classes have actually undergone some chemical alterations. This would mean that altered particles as here defined are simply normal coral particles which have been heated up to and above melting and boiling temperatures.

* This group of eighteen particles was not selected at random. Attempts were made to secure active spherical particles; however, a mixture of spherical and irregular particles were obtained.

[13] W. WILLIAMSON, JR., USNRDL-TR-152 (1957).

[14] C. E. ADAMS, USNRDL. Personal communication (1958).

Vol. 15 1960

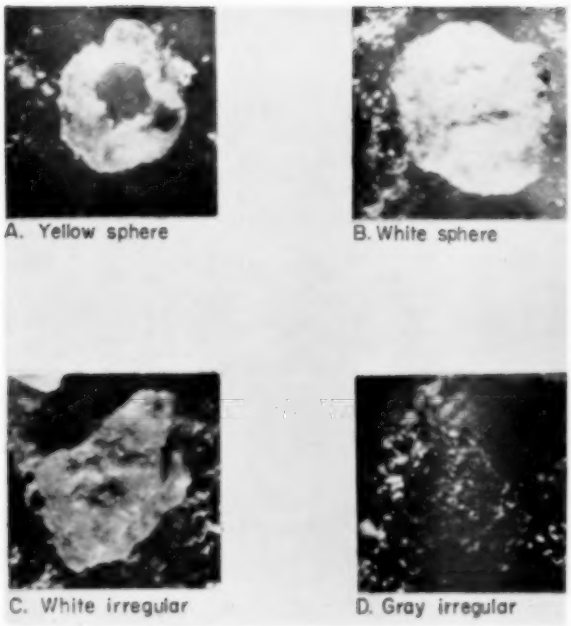

FIG. 1.—Particle types observed in the Barge sample. Altered particles are shown in A and B, Unaltered particles in C and D.

Vol.
15
1960

The only exception to the general classifications adopted above were a few particles typed as yellow irregular (*YI*) but which were easily recognized as portions of broken spheres. These were, therefore, altered particles.

RESULTS

The majority of the analytical data obtained are presented in three tables and one figure. One table includes all counting and radiochemical data for all individual particles studied. The figure shows the activities of a large number of particles selected at random from the Barge sample. Additional data for the Barge sample are given in the second and third tables. Data describing decay and γ-spectra are presented later in this report in the section where the counting and radiochemical results are discussed. This method of presentation was adopted since the primary purpose of the decay and spectral data was to aid in the interpretation of the counting and radiochemical results.

In the listings of data, particles are described on the basis of colour and shape. A pictorial representation of several particle types is provided in Fig. 1.

Radiochemical and counting data for individual particles

Table 1 includes data for particles which were selected for individual analysis. Measurements of ^{140}Ba and ^{89}Sr content are expressed as *R* values. Well counter and GIC assays are given at times of measurement in units of counts per minute (c.p.m.) and milliamperes of ionization current (mA), respectively. Limits of reliability are indicated by the number of significant figures and are discussed later in the report.

Physical and counting data for the Barge sample

Table 2 presents weight and activity values for the Barge sample. The calculations for total fissions were based on empirical GIC values for milliampere/fission vs. time observed on a gross sample of fall-out collected on the island.

Counting data for individual particles selected from the Barge sample

Data for a number of particles from the Barge sample have been presented in Table 1. An additional number of particles were selected from three size fractions and were measured in the γ-well counter. A total of 639 particles were removed from the three indicated size ranges. Of this total, 211 particles were uncertain as to description and therefore were not typed. The activities of the remaining 428 particles are given in Table 3 and are shown in Fig. 2. Since decay corrections were small over the periods of measurement, the activities may be considered at H + 382 hr.

DISCUSSION

Data have been presented for radiochemical analyses of a number of individual fall-out particles. Analyses of these particles were possible because they contained radionuclides from approximately 10^{10} fissions (or more).

Some discussion of particle types has been presented earlier. It was stated that the coral particles could be grouped into two broad categories (classes)—altered and unaltered, depending upon whether the physical appearance of the coral particles resembled a spherical or flaky (altered) shape or an angular or irregular (unaltered) shape. Division of the particles into two such broad classes was convenient in that it permitted the data to be inspected for gross differences. However, it should be realized that such divisions are not sharply bounded since differences exist between

TABLE 1.—COUNTING AND RADIOCHEMICAL RESULTS FOR INDIVIDUAL PARTICLES

Source	Sample no.	Description	WC assay		GIC assay		Total fissions (10^{19})	^{140}Ba *R* value	^{89}Sr *R* value	Weight (mg)
			Value (10^6 c.p.m.)	TSD (hr)	Value (10^{-11} mA)	TSD (hr)				
Ship	1	*WI*	0·358	70	50	70	0·67			
	2	*WS*	0·0387	70	7	70				0·0094
	5	*YS*	0·291	70	25	70	0·72		0·015	
	6	*YS*	0·527	70	41	70	1·4			
	8	*YI*	0·255	71	26	71	0·80	0·12	0·030	
	11	*WI*	0·0125	71	—	—				
	13	*WI*	0·217	71	26	70	0·67	0·27	0·075	
	29	*WI*	0·0411	72	2	71				
	73	*WI*	0·237	73	19	73	0·49		0·15	
	80	*YS*	0·210	74	19	73	0·79		0·19	
	88	*WI*	0·266	75	29	74	0·34		0·24	
	96	*WI*	0·0173	75	3	74				
	128	*WS*	0·172	75	16	74				
Island	148	*GI*	3·61	98	432	98	6·4	2·3	0·54	16·440
	149	*I*	1·71	99	183	99				6·110
	150	*WI*	3·52	99	172	99	1·9	2·2	1·1	8·600
	151	*WI*	2·48	100	316	100	3·7	3·4	0·66	8·170
	152	*YI*	8·80	100	497	100	22	0·12	0·027	2·196
	153	*WI*	0·0361	103	3	103				3·530
	154	Metal	0·0211	103	3	103				0·303
	155	*I*	3·33	103	257	103	2·6	0·76	0·34	3·200
	156	*WI*	1·12	104	141	103	1·0	3·1	1·5	4·123
	157	*YS*	1·17	104	108	104				
	158	*I*	0·0342	104	4	104				0·171
	159	*S*	19·3	105	1320	105	75	0·015	0·0025	2·246
	160	*GI*	0·751	105	95	105	0·64	3·4	1·5	0·920
	161	*GI*	0·208	105	24	105				1·883
	162	*WI*	0·830	105	116	105	0·87			0·872

TABLE 1.—COUNTING AND RADIOCHEMICAL RESULTS FOR INDIVIDUAL PARTICLES (*Contd*)

Source	Sample no.	Description	WC assay		GIC assay		Total Fissions (10^{16})	^{140}Ba *R* value	^{89}Sr *R* value	Weight (mg)
			Value (10^6 c.p.m.)	TSD (hr)	Value (10^{-11} mA)	TSD (hr)				
Island	163	*WS*	6·75	119	511	119	17	0·17	0·026	3·302
	164	*WI*	0·114	119	16	119				0·393
	165	*WI*	0·110	119	12	119				0·668
	166	*GI*	0·0943	119	10	119				2·738
	167	*GI*	0·480	119	64	119				1·672
	168	*GI*	0·207	119	26	119				1·137
Barge (prior to sieving)	165W	*YS*	17·5	239	1090	239				6·90
	166W	*YS*	37·8	239	3300	239				17·3
	167W	*I*	3·42	239	260	239				40·1
	168W	*YS*	36·6	239	2720	239				8·70
	169	*I*	0·101	239		239				11·9
	170	*WI*	1·94	239	323	239	16	1·5	0·42	48·3
	171	*S-*	6·30	239	244	239				
	172	*S*	16·7	239	895	239				
	173	*I*	2·23	239	298	239				11·4
	174	*S*	24·3	239	1400	239				7·10
	175	*S*	9·05	239	490	239				2·50
	176	*GI*	0·444	239	51	239				48·8
	177	*S*	2·63	239	164	239	49	0·026	0·0080	1·73
	178	*I*	1·76	239	189	239				388·0
	179	*YS*	6·72	239	465	239				5·10
	180	*I*	1·71	239	199	239				457·0
	181	*YI*	28·0	239	1720	239				25·8
	182	*I*	0·071	239	—					9·00
Barge (after sieving)	Particles size range 500–1000 μ	*WI*	1·07	532	226	481	44	0·70	1·19	11·34
		YS	2·79	532	360	481	190	0·024	0·017	2·76
		WS	1·64	532	199	481	150	0·013	0·016	1·76

particles in a single class. Some differences were observed in this investigation. Others are implied in WILLIAMSON's[13] data, which indicates that the yellow spherical particles were slightly more radioactive and more dense than the white spheres. These latter indications were in qualitative agreement with the count data of this investigation

TABLE 2.—WEIGHT, ACTIVITY AND FISSION VALUES FOR THE SIZED FRACTIONS FROM THE BARGE SAMPLE

Size range (μ)	Weight		GIC assay			Fissions	
	(g)	Per cent of total	Value* (10^{-2}mA)	Per cent of total	Specific activity* (10^{-3}mA/g)	Total (10^{14})	Per gramme (10^{14})
1000	37·70	41·8	1·08	15·8	0·0286	21	0·56
500–1000	41·91	46·4	3·14	46·0	0·0749	60	1·4
250–500	4·97	5·5	1·35	19·8	0·272	26	5·2
100–250	3·51	3·9	0·734	10·7	0·209	14	4·0
50–100	0·80	0·9	0·155	2·3	0·194	3·0	3·8
50	1·38	1·5	0·371	5·4	0·269	7·1	5·1
Total	90·27		6·83		0·0757	131·0	1·5

* at H + 262 hr

TABLE 3.—ACTIVITY AT H + 382 hr OF BARGE SAMPLE PARTICLES FROM SIZED FRACTIONS

Size range (μ)	Particle type	Number of particles	Total WC activity at H + 382 (10^6 c.p.m.)
500–1000	*YS*	11	14·5
	LYS	10	10·8
	WS	11	7·84
	WI	57	7·31
	GI	21	1·22
250–500	*YS*	43	16·9
	LYS	18	6·25
	WS	24	3·63
	WI	156	7·29
	GI	12	0·0913
100–250	*YS*	17	3·62
	LYS	4	0·450
	WS	9	0·611
	WI	33	0·277
	GI	2	0·00194

(see Table 3 and Fig. 2) and with chemical spot tests which were made for iron and which consistently indicated greater amounts of iron in the yellow samples than in the white.

It is possible that additional types of particles existed and were not observed in all samples. For example, the shipboard personnel estimated that 13 per cent of the particles from the greased trays were of a delicate flaky or aggregated composition as

Vol. 15 1960

opposed to the spherical and irregular particles. Flaky particles were not observed in the Barge and Island samples, very possibly due to the sampling methods which in some cases included sieving. Uncertainties of this nature, the physical appearance of the particles, and inspection of the data led to the concept of two broad classes of fall-out particles.

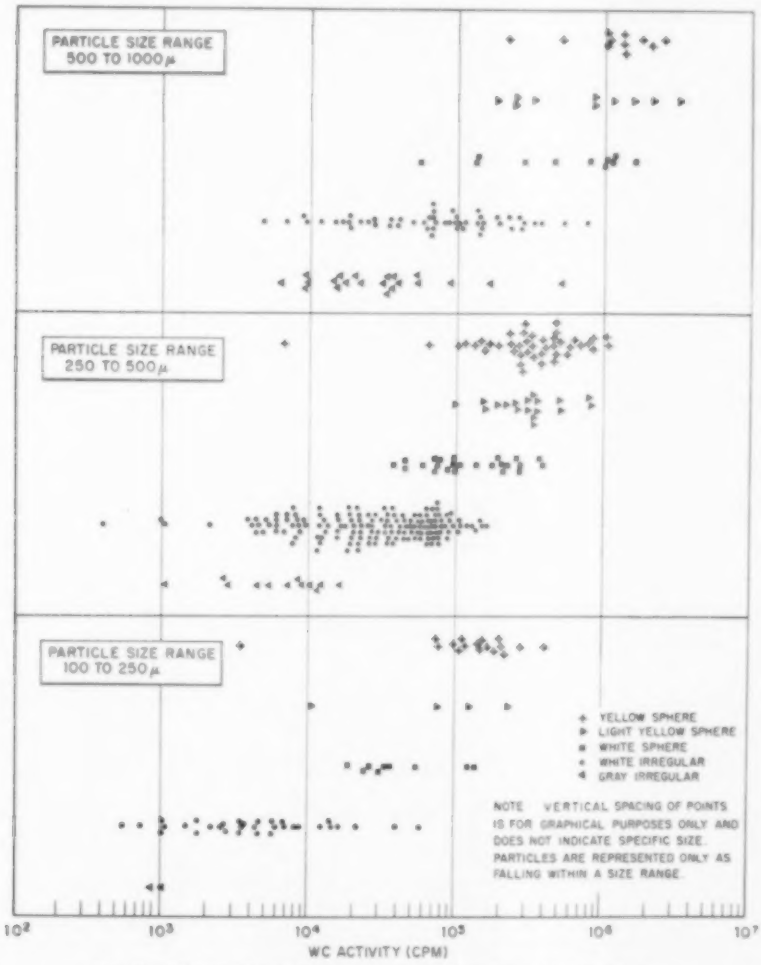

FIG. 2.—WC activity of Barge sample particles from sized fractions. H + 382 hr.

In order to investigate the data for differences in radioactive composition three assumptions were made as follows:

(1) Particles may be classified into two categories, physically altered or physically unaltered;

(2) Particle radionuclide composition depends only on particle category. Thus, although the numbers and size ranges of the two categories of particles may vary with

time and point of collection, particles of the same category have similar radioactive compositions.

(3) Fractionation of the reference nuclide, ^{99}Mo, is small compared to the observed differences between particle categories.

In view of these assumptions an inspection of the data in Table 1 immediately reveals differences in the radioactive composition of the two classes of particles observed. These differences are shown in Figs. 3, (a), (b), (c) and Table 4. The figures

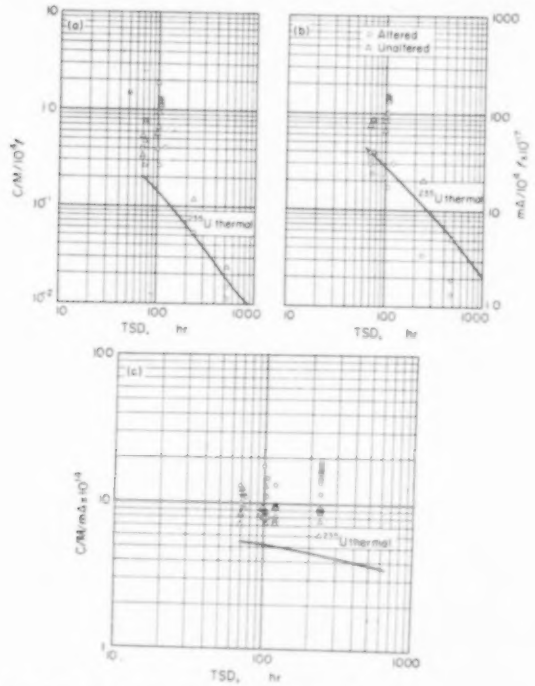

FIG. 3.—Activity ratios as a function of time of measurement.
(a) Well counter
(b) γ-ionization chamber
(c) Ratio WC/GIC

show the time dependent activity ratios WC c.p.m./10^4f, mA/10^4f, and WC c.p.m./mA as a function of time of measurement for both altered and unaltered samples and also show, for comparison, similar data obtained in calibration runs with enriched ^{235}U in which the ^{239}Np contribution was low. Deviations of the values from the latter curve indicate the combined effects of fractionation, fission yield variations and induced activities. The relative positions of the points to each other clearly show the differences in the time dependent activity ratios for the two types of particles. The mean values for these ratios at the various times of measurement are given in Table 4 along with average values for time independent quantities which were also derived from the individual particle data in Table 1. The number of determinations and standard deviations of the mean values are also given in Table 4.

The data of Table 4 show that the value of fissions/gramme was much larger in the altered particles than in the unaltered particles. The R value data indicates that the

Vol. 15 1960

altered particles were markedly depleted in ^{140}Ba–^{140}La, whereas the unaltered particles were enriched in ^{140}Ba–^{140}La. Depletion of ^{89}Sr occurred in altered particles and, possibly, in unaltered particles. The *R* values are shown graphically in Figs. 4(a) and 4(b) in which the numbers of atoms of each nuclide are plotted vs. the number of ^{99}Mo atoms found in the same sample. The straight lines represent estimated fission yields for ^{140}Ba and ^{89}Sr. Product to fission ratios for ^{239}Np did not exhibit as wide a

TABLE 4.—MEAN VALUES FOR SEVERAL QUANTITIES FOR ALTERED AND UNALTERED PARTICLES

Quantity	Time (H + hr)	Particle category			
		Altered		Unaltered	
		No. of samples	Value	No. of samples	Value
fiss/g($\times 10^{15}$)	—	6	3·8 ± 3·1	9	0·090 ± 0·12
^{140}Ba–*R* value	—	5	0·090 ± 0·068	8	2·1 ± 1·2
^{89}Sr–*R* value	—	7	0·018 ± 0·010	10	0·65 ± 0·17
WC c.p.m./10^4f	71	4	0·34 ± 0·06	4	0·53 ± 0·19
WC c.p.m./10^4f	105	3	0·35 ± 0·08	7	1·1 ± 0·4
WC c.p.m./10^4f	239	1	0·054	1	0·12
WC c.p.m./10^4f	532	2	0·013	1	0·024
mA/10^4f($\times 10^{-17}$)	71	4	30 ± 5	4	59 ± 24
mA/10^4f($\times 10^{-17}$)	105	3	24 ± 7	7	109 ± 31
mA/10^4f($\times 10^{-17}$)	239	1	3·4	1	20
mA/10^4f($\times 10^{-17}$)	481	2	1·7	1	5·1
WC c.p.m./mA($\times 10^{14}$)	71	5	11 ± 1	4	9·3 ± 2·0
WC c.p.m./mA($\times 10^{14}$)	105	4	14 ± 3	13	8·6 ± 1·5*
WC c.p.m./mA($\times 10^{14}$)	239	10	16 ± 2	6	8·2 ± 1·3

* Does not include one value, 20·5 × 10^{14} for sample no. 150.

variation between particle class as either of the fission products studied. The p/f ratios obtained from individual particles were comparable to standard cloud sample values† but, on the average, were higher in samples of unaltered composition.

Other measurements were made on three separate groups of particles from the Barge sample, which confirm the noted differences between altered and unaltered particles. The first group all consisted of *WI* (i.e. unaltered) particles; the second and third groups consisted of all *YS* and all *WS* (i.e. altered particles), respectively. The data obtained are shown in Table 1. Once again, a greater number of fissions were associated with altered particles and, again the *R* values show marked depletion of ^{140}Ba–^{140}La and ^{89}Sr in the altered particles.

The above data establish differences according to particle class. Although additional data would be required for quantitative assessment of these differences it was possible to study some of their effects by observaton of gross decay rates, γ-ray spectra, fission per gramme values, and *R* values.

† Filter samples collected by aircraft flown through the cloud and often used as reference samples.

(a) *Decay measurements.* Gross decay measurements were carried out in the γ-well counter for two altered samples (no. 6 and no. 128) and two unaltered samples (no. 1 and no. 96). The curves for samples no. 1 and no. 6 are shown in Fig. 5(a). The pronounced change in decay rates after 1000 hr for the altered samples as compared to the unaltered samples was verified by counts taken on a number of individual particles at H + 400 and H + 7100 hr. The mean ratio of the late count divided by the early count for thirty-seven samples of the altered category was 0·015 ± 0·008

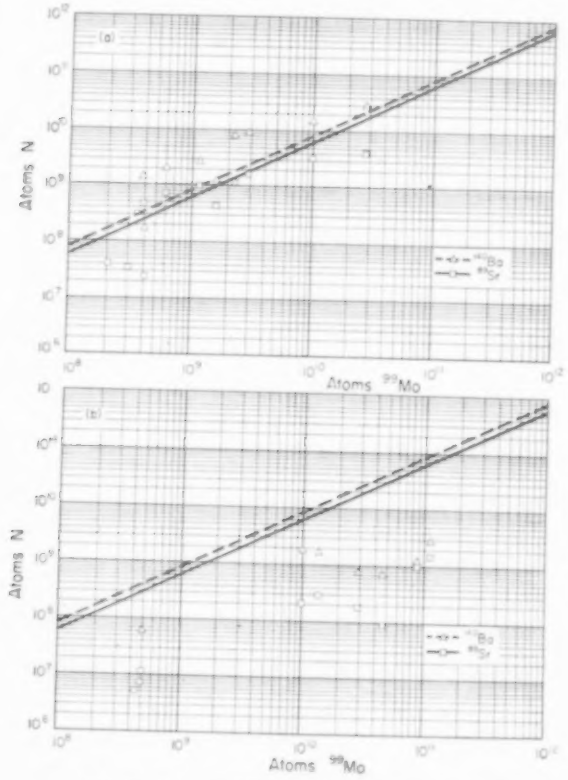

FIG. 4.—Atoms of ^{89}Sr and ^{140}Ba vs. atoms of ^{99}Mo.
(a) Unaltered particles
(b) Altered particles

or approximately twice the corresponding ratio of 0·0085 ± 0·0042 found for sixty-five unaltered samples. These values are in good agreement with decay curve values from Fig. 5(a) which give 0·015 and 0·0076 respectively for the altered (no. 6) and unaltered (no. 1) samples. The differences in decay rates are again shown in Fig. 5(b) where the decay curves are plotted in terms of 10^4 fissions. Plots of the type shown in Fig. 5(b) should coincide for samples with equivalent radioactive compositions.

(b) *γ-Ray spectra.* In addition to rates of decay, the effects of differences in nuclide composition are shown by comparison of γ-spectra of altered and unaltered particles taken at various times after detonation. These spectra are shown in Fig. 6. Although differences are readily observed, the complex pulse height distributions are not easily

Vol. 15 1960

resolved without extensive radiochemical data. For example, in Fig. 6, the 0·1 MeV photons from ^{239}Np are considerably more abundant in particle no. 6 than in no. 1. The result is a more rapid decay at early times for particle no. 6 as shown earlier in

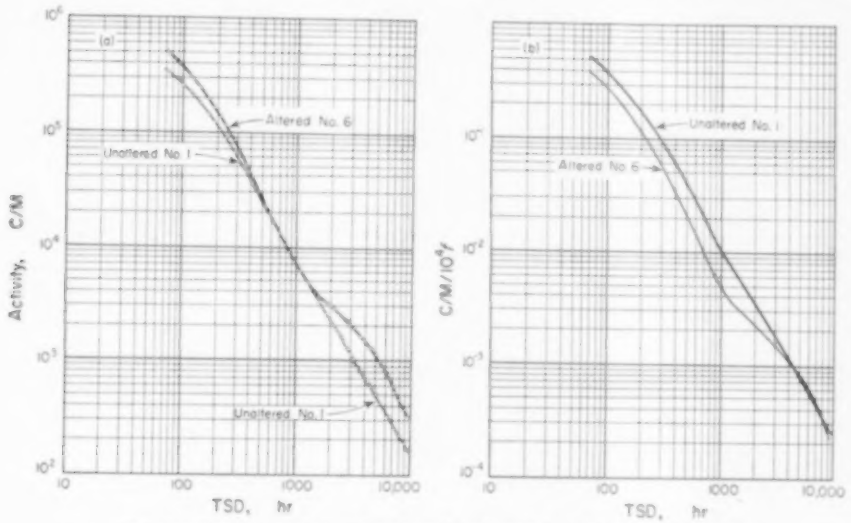

FIG. 5.—WC decay of altered and unaltered particles. (a) Observed activity. (b) Observed activity per 10^4 fissions.

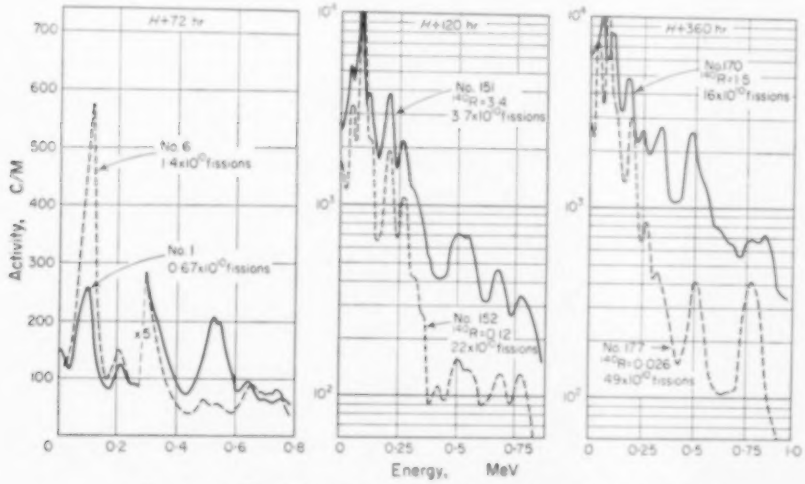

FIG. 6.—γ-Pulse height distributions of altered (nos. 6, 152, 177) and unaltered (nos. 1, 151, 170) particles.

Fig. 5(a). The reasons for differences in decay rates at about H + 2000 hr, however, are not readily apparent on the basis of the observed γ-spectra shown in Fig. 6.

Additional differences are shown by comparison of the total fission values for the samples in Fig. 6 (Particles nos. 151, 152, 170 and 177) with the γ-spectra above 0·4 MeV. These spectra clearly indicate a relatively higher abundance of photons

above this energy in particles of unaltered composition. This is in good agreement with measured R values for the 140 mass-chain which were over an order of magnitude higher in the unaltered than in the altered particles.

(c) *Fissions per gramme of fall-out.* Table 4 reports mean fissions per gramme of fall-out for those samples which were weighed and analysed for total fissions. Using the activity ratios (WC c.p.m./10^4f, mA/10^4f) given in Table 4 it was possible to compute the total fissions for a number of samples which had been weighed and counted but not analysed for total fissions. The computations also include all samples which were analysed for total fissions except for the combined sample *WI.** The particles were grouped according to class and the calculations made on the basis of activity ratios for each class as given in Table 4. The mean values for fissions/gram differ by approximately a factor of 100. (Altered—$4{\cdot}2 \pm 2{\cdot}7 \times 10^{14}$; Unaltered—$0{\cdot}033 \pm 0{\cdot}035 \times 10^{14}$). This difference when compared with the data given earlier in Table 2 indicates that a very significant fraction of the total activity in the Barge sample was from particles of the altered category. The latter observation is in agreement with the individual samplings presented in Table 3 and Fig. 2 which show that approximately 80 per cent of the well counter activity at H + 382 hr was from the altered samples and an even higher percentage of the total fissions.

(d) *R values.* With respect to fractionation of radionuclides it has long been accepted that the mass 89 and mass 140 chains which exist for long time periods as noble gases, halogens and alkali metals† would condense late and therefore disproportionate with respect to less volatile elements. On the basis of long-lived gaseous precursors it would be predicted that the altered or melted particles would exhibit low R values for both chains, with the eighty-nine the smaller of the two. This was verified by the mean R values given in Table 4 and which were 0·090 and 0·018 for the 140 and eighty-nine chains, respectively. The corresponding values for the unaltered particles of 2·1 and 0·65 indicate that this latter class of particles may be important as a scavenger of these nuclides.

It is also of interest to compare R values obtained in this study with values obtained on gross fall-out samples collected from the Atoll. The latter data gave ^{140}Ba R values and ^{89}Sr R values of 0·10 and 0·04 respectively.[15] The low R values for the gross sample from Bikini Atoll are similar to R values obtained with altered particles and suggests a close-in fall-out composed primarily of altered particles. This suggestion is supported by the Barge sample fission/gramme data (described above).

VALIDITY OF THE DATA

The data presented in this report are of three distinct types. These are weight determinations; activity measurements (in terms of instrument response, e.g. milliamperes, counts); and radiochemical determinations for total fissions and R values.

The weight determinations were carried out with an accuracy and precision of approximately $\pm 5\mu$g. Thus, the majority of the weight determinations were made to better than ± 1 per cent.

* The fission/gramme value for this sample, $0{\cdot}39 \times 10^4$, yielded a deviation from the mean of approximately seven times the probable error of the mean and was not used in the computations.

† ^{140}Ba is formed by the decay of the radioelements ^{140}Xe (16 sec half-life) and ^{140}Cs (66 sec half-life); ^{89}Sr is formed by the decay of the radio-elements ^{89}Kr (3·16 min half-life) and ^{89}Rb (15·4 min half-life).

[15] P. D. LARIVIERE, USNRDL. Personal communication (1957).

Vol. 15 1960

With few exceptions all determinations of activity by γ-well counting (WC) were carried out with a statistical precision of ± 3 per cent or better. The ionization chamber measurements (GIC) were made with a precision dependent upon the total activity. For samples reading greater than 10^{-9} mA the precision was better than ± 5 per cent and decreased from this value to approximately ± 20 per cent for samples which gave readings of $2\times$ background (17×10^{-11}mA).

Experience with large numbers of samples has shown that the precision of the various radiochemical methods used in this study varied from ± 10 to ± 15 per cent. Since measurements of total activity were usually made with a far greater precision than the radiochemical analyses, the errors in the computations of the various activity ratios in terms of fissions were almost entirely dependent on the errors in radiochemical analysis. The accuracy of the radiochemical determinations were generally estimated as correct to ± 25 per cent but may have been as low as ± 50 per cent for samples of low activity.

However, it is an unfortunate circumstance of experiments of this type that a large number of variables, many uncontrolled or unknown, exist which could introduce errors greater than those present in the methods of analysis. It is also generally true that little is known concerning the magnitude of such errors. Among errors of this kind may be listed the following:

(1) Alteration of sample by collector, in transit, or in sampling process;

(2) Non-random or biased selection;

(3) Assumptions concerning reference standards.

Concerning the third point it is customary to base calculations for total fissions on the measured number of atoms of the reference nuclide, ^{99}Mo. Although comparisons made on the basis of the latter quantity alone are valid it is apparent that estimates for total fissions or fractionation behaviour of additional isotopes are actually based on the distribution of the reference nuclide throughout the fall-out samples.

CONCLUSIONS

A primary conclusion is that the analysis of individual particles created by at least one type of detonation is entirely feasible. This feasibility was established since individual particles which represented approximately 10^{10} or more fissions were obtained. Thus it was possible to make quantitative measurements of the radioactivity of such particles.

Physical inspection of the fall-out particles revealed several types of particles, each of which usually could be classified into one of two general divisions. The first particle class was made up of spherical or flaky particles. These were designated altered particles inasmuch as they represented an obvious physical alteration of normal coral particles. The second class consisted of angular or irregular particles and were designated unaltered particles. The most significant differences in the two classes were found to be in the amount and nature of the radioactivity associated with the particles. Based on the assumptions of (a) a radionuclide composition dependent only on particle class and not time or point of collection and (b) no serious disproportionation of the reference nuclide, ^{99}Mo, by particle class it was found that the two particle categories differed in several respects among which were the following:

(1) On the basis of simple arithmetic means the altered particles were approximately 100 times higher in terms of fissions per gramme of total mass than were the unaltered.

(2) The R values for ^{140}Ba and ^{89}Sr were over an order of magnitude lower in the altered particles than in the unaltered particles.

(3) Inspection of ^{140}Ba R values and comparison of total fission values with γ-spectra above 0·4 MeV, indicated a relatively higher abundance of photons above this energy in particles of unaltered composition.

(4) In a sample collected near the site of detonation a very high percentage of the total fissions were due to particles of the altered category.

(5) Decay rates for the altered and unaltered particles differed markedly at times less than H + 100 and greater than H + 1000 hr.

Some discussion and possible explanations for the observed data has been given earlier. As a result, it is proposed that fall-out data obtained on gross particulate samples, where possible, should be evaluated on the assumption of sample compositions consisting of varying percentages of altered and unaltered fall-out particles as defined in this report.* That is, the data be inspected to determine if fractionation effects, differences in γ-energy flux per fission, etc. may be attributed to the relative numbers of altered and unaltered particles. Presentations of single particle data in terms of fissions/gramme, R values, rates of decay, γ-spectra and activity ratios should aid in the interpretation of gross sample values. The individual particle information may also be of value in fall-out model derivations and predictions and in particle formation theory.[2]

Acknowledgements—Helpful discussions are acknowledged with P. D. LARIVIERE and with S. BAUM, C. F. MILLER, T. TRIFFET and L. B. WERNER, all of the USNRDL.

* Preliminary calculations carried out by P. D. LARIVIERE, USNRDL, and the authors indicate that R values for gross samples are calculable from single particle radiochemical data and knowledge concerning the relative numbers of altered and unaltered particles.

Vol. 15 1960

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THE EFFECT OF AMINE SCAVENGERS ON PRODUCTS OF NEUTRON IRRADIATION OF ORGANIC HALIDES

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(*Received* 20 *October* 1959)

Abstract—The mechanism of the effect of primary amines on retention in neutron irradiated organic halides has been investigated. The evidence indicates that amines may act as radical scavengers.

IN early work on the Szilard–Chalmers reaction in organic halides LU and SUGDEN found that addition of amines such as aniline, dimethylaniline, diethylamine or *m*-phenylene diamine caused a marked reduction in the percentage of radioactive halogen atoms retained in organic combination.[1] These authors suggested that the following type of reaction may account for the increased percentage of radioactive halogen atoms found to be stabilized in inorganic forms when an amine is present during irradiation:—

$$R + X^* + NH_2R' \rightarrow R'NH_2R^+ + X^* \qquad (1)$$

where R is the radical formed after escape of the radioactive halogen atom X*, from the irradiated compound RX after neutron capture. The authors also suggested that a similar reaction may occur when the RX* bond is not ruptured by the recoil but contains enough vibrational energy to bring about the reaction:

$$RX^* + NH_2R' \rightarrow R'NH_2R^+ + X^* \qquad (2)$$

LIBBY[2] explained the so-called "aniline effect" by assuming that a Menschutkin reaction of the type (2) above occurred, but that it took place with freshly reformed RX* molecules before they could cool by loss of excess vibrational energy to the "cage" walls. RX* molecules were considered by LIBBY as being reformed largely on the basis of his postulated "billiard-ball" collision mechanism.

It would seem, however, that another possibility exists for explaining the aniline effect, which would make the amines a more interesting class of substances for studies in hot atom chemistry. Amines are known to be powerful inhibitors of chain reactions such as oxidations of organic substances.

It has been suggested[3] that since the amines have a weakly bound hydrogen atom, the peroxide radical $RO_2\cdot$ formed in the chain process could abstract an H atom from the amine inhibitor, forming an aniline radical which is incapable of continuing the chain. It may be, therefore, that radicals formed by the "hot" X* atom in irradiated halides are similarly scavenged by amines. Retention would thus be lowered, since X* atoms on cooling would find less radicals with which they could combine.

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[1] C. LU and S. SUGDEN, *J. Chem. Soc.* 1273 (1939).
[2] W. F. LIBBY, *J. Amer. Chem. Soc.* **69**, 2523 (1947).
[3] N. N. SEMENOV, *Some Problems in Chemical Kinetics and Reactivity* (Translated by M. BOUDART), Vol. 1 pp. 188–189. Princeton University Press (1958).

If this latter explanation of the aniline effect were true then amines would act in a similar way to that of elementary halogens, whose effect in reducing retention in irradiated organic halides has been ascribed to radical scavenging.[1] The experiments here reported were done to assess the similarity of the effects of amine and halogen scavengers on the organic retention in irradiated organic halides.

EXPERIMENTAL

Methylene bromide, bromoform and bromobenzene samples were purified shortly before irradiation by shaking for 2 hr with concentrated sulphuric acid, followed by prolonged washing with water, extracted with 5 per cent aqueous sodium carbonate solution and then with 5 per cent sodium thiosulphate, followed again by prolonged washing with water. Samples were then dried by contact with phosphorus pentoxide, with periodic shaking, and finally distilled from phosphorus pentoxide through an 80 cm empty-tube vacuum-jacketed column, collecting a 60 per cent middle cut of the fraction coming over at the appropriate temperature. Samples were stored in dark glass bottles, the period before use being only 2–3 hr in order to minimize decomposition.

Irradiation of 30–50 ml samples was done in the dark in glass vessels in a water moderator at an average distance of 5 cm from a 500 mg Ra/Be source, for periods of 2–17 hr.

To determine total retention of 4·5 hr ^{80}Br activity in organic combination, the irradiated halide was extracted with an equal volume of 5 per cent aqueous sodium thiosulphate solution containing 0·03 per cent sodium bromide carrier. After waiting for 2 hr to allow effective decay of 18 min ^{80}Br activity formed during the irradiation period, the 18 min activity in equilibrium with the 4·5 hr ^{80}Br was measured in each phase, using a thin-walled glass immersion counter with appropriate density corrections.

In experiments to determine the distribution of activity in various products of irradiation of methylene bromide, appropriate carriers were added and then separated by distillation. To determine the amount of activity in methyl bromide, 60 ml of this compound were added as carrier to 60 ml of irradiated methylene bromide. The methyl bromide was distilled off at atmospheric pressure, without a column, the first and last 10 per cent being rejected. It was found that under all conditions only 4·5–5·1 per cent of the total activity came over with the methyl bromide, so that this fraction has been omitted from the results shown in Table 1. The results of Table 1 were obtained as follows: 60 ml of methylene bromide were irradiated for 17 hr. Inorganic Br* was removed by extraction with thiosulphate solution with bromide carrier. A 10 ml portion of the extracted halide was then set aside for determination of total activity in organic combination. To 50 ml of the remainder were added 40 ml bromoform and 5 g carbon tetrabromide as carriers, and the mixture distilled through an 80 cm empty-tube vacuum-jacketed column. Approximately 20 per cent heads and 20 per cent tails of the methylene bromide and bromoform fractions were rejected, the middle cuts being taken for activity measurements after standing for 2 hr to allow decay of initial 18 min ^{80}Br activity. At the end of the bromoform tail when the total volume of distilled bromoform was approximately equal to the amount of bromoform added, the temperature began to rise slowly and when it had reached 154–155°C the distillation was interrupted so as to prevent too extensive decomposition of the carbon tetrabromide. The contents of the distillation flask were then dissolved in chloroform and the activity of this fraction measured after allowing it to stand for 2 hr. This fraction is shown as "CBr_4" in Table 1, and in addition to CBr_4 may contain higher boiling point 2-carbon compounds. In columns 3,4,5,6 of Table 1 activities are expressed as percentages of total activity measured in a separated aliquot of the organic phase.

Irradiated bromoform was fractionated by a procedure similar to that described for methylene bromide.

RESULTS AND DISCUSSION

When an elementary halogen is added in increasingly large amounts to an organic halide before irradiation, there is at first a rapid drop in organic retention, after which further addition of halogen reduces the yield relatively little. That part of the organic retention which is relatively insensitive to the concentration of added halogen has been

[1] J. E. WILLARD, *Ann. Rev. Nucl. Sci.* **3**, 193 (1953).

Vol. 15 1960

attributed to so-called "hot" processes, such as combination of radioactive atoms with organic radicals immediately after the atoms have cooled and before they have had opportunity to diffuse about the system as thermal atoms, or by billiard-ball type

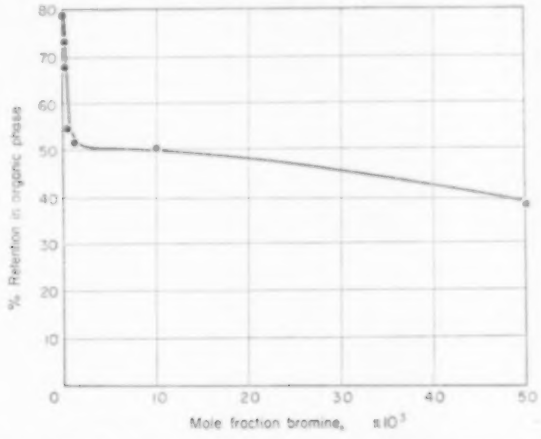

FIG. 1.—Effect of bromine on retention in irradiated methylene bromide as a function of concentration.

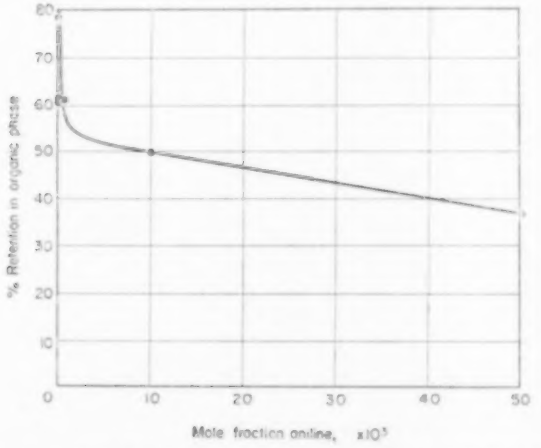

FIG. 2.—Effect of aniline on retention in irradiated methylene bromide as a function of concentration.

collisions, or by high activation energy reactions.[5] That part of the organic retention which is relatively sensitive to the concentration of added halogen has been attributed to so-called thermal processes, such as combination of the radioactive atom with a radical formed in the cooling process but which it encounters again only after many thermal collisions with other species, or radical formation by abstraction reactions.[5]

Figs. 1–3 show the very close similarity between the effects of aniline, n-butylamine

[5] S. GOLDHABER and J. E. WILLARD, *J. Amer. Chem. Soc.* **74**, 318 (1952); M. M. MILMAN and P. F. D. SHAW, *J. Chem. Soc.* 1303, 1317, 1326 (1957).

and bromine on the retention of Br* in methylene bromide after the reaction $^{79}Br(n, \gamma)^{80}Br$, as a function of the concentration of the added substance. A check was made that trivial chemical effects were not involved by adding aniline or n-butylamine after

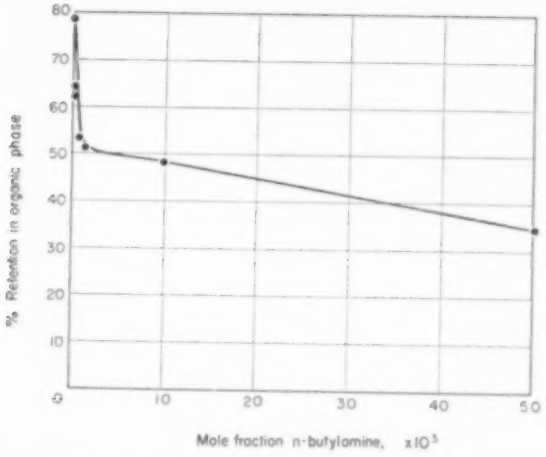

FIG. 3.—Effect of n-butylamine on retention in irradiated methylene bromide as a function of concentration.

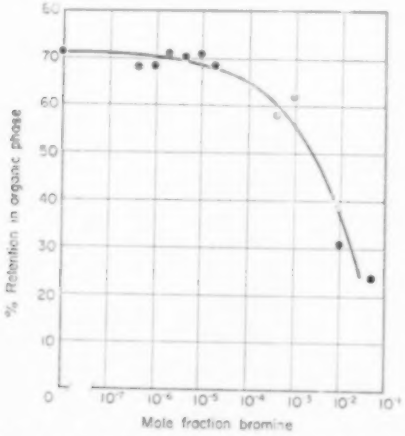

FIG. 4.—Effect of bromine on retention in irradiated bromobenzene as a function of concentration.

irradiation, but as in the experiments of LU and SUGDEN no significant effects on the retention were observed.

Figs. 4–6 show the effects of aniline, n-butylamine and bromine on the retention of ^{80}Br in irradiated bromobenzene. If these results are plotted on a linear abscissa then closely similar curves resembling those of Figs. 1–3 in shape are obtained. From Figs. 4–6 the effects of very small concentrations of the added substances can be seen. The curves have a general similarity.

It thus seems that as in the case of the halogen scavengers the primary amines show

Vol. 15 1960

a region in which the retention is very sensitive to concentration of scavenger (up to ca. 10^{-3} mole fraction) and a region of markedly lower sensitivity to scavenger concentration (above 10^{-3} mole fraction). This evidence, bearing in mind the close similarity of the curves obtained for amines and bromine, strongly suggests that the amines are acting as radical scavengers by virtue of their labile hydrogen in a similar way to their

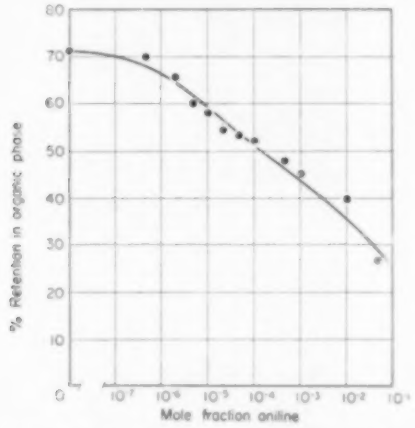

FIG. 5.—Effect of aniline on retention in irradiated bromobenzene as a function of concentration.

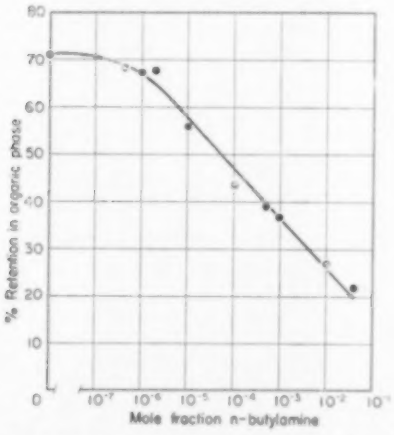

FIG. 6.—Effect of n-butylamine on retention in irradiated bromobenzene as a function of concentration.

behaviour in inhibiting chain reactions. In turn this finding tends to support the previously advanced explanations of the halogen scavenger curves, in which the initial rapid fall of retention is considered as due to scavenging of radicals which would otherwise be encountered by the active atom in an event leading to organic retention, while the insensitive portion of the curve is ascribed to hot processes.

The above evidence does not support the mechanisms postulated by LU and SUGDEN and by LIBBY to explain the "aniline effect". These mechanisms do not predict a rapid decline in retention for small amounts of added amine, followed by a

more insensitive portion of the curve. A more even decline of retention with rising amine concentration is rather to be expected.

Table 1 shows the distribution of organically retained ^{80}Br in fractions separated from irradiated methylene bromide by distillation, as described. Most of the retained activity is in the irradiated substance, smaller amounts being in $CHBr_3$ and still smaller amounts being in CBr_4 (and other high boiling point substances). Addition of bromine reduces the percentage of events leading to retention in the irradiated molecule from 43 per cent on average to 35 per cent, whereas the retentions in $CHBr_3$ and "CBr_4" are relatively much more markedly reduced. This is exactly the sort of behaviour which is to be expected if a considerable proportion of the events giving organic retention were due to the hot process of billiard-ball collisions,[2] the remainder being due to radical mechanisms.

Billiard-ball processes can only lead to reformation of the parent molecule, and these may account for the 35 per cent of events which yield radioactive molecules of the parent type even in the presence of 0·01 mole fraction of bromine scavenger. Radical mechanisms can yield $CHBr_3$ and CBr_4 by reactions such as

$$CH_2Br_2 \text{ (inelastic collision)} \rightarrow CHBr_2\cdot(+Br^*) \rightarrow CHBr_2Br^* \qquad (3)$$

$$CH_2Br_2 \text{ (inelastic collision)} \rightarrow CBr_2\cdot\cdot\ (+Br^*)\ CBr_2Br^*(+Br)\ CBr_3Br^* \qquad (4)$$

and such a process will be relatively more sensitive to addition of scavengers, thus accounting for the relatively more drastic drop in retention in the $CHBr_3$ and "CBr_4" fragments when bromine is added.

From Table 1 it can be seen that aniline has a similar effect to bromine and this once more suggests that aniline is also acting as a radical scavenger.

Table 2 shows the distribution of organically retained ^{80}Br in fractions separated from irradiated bromoform. The results in this table further support the conclusions drawn in the previous two paragraphs.

It would seem from the results obtained from bromine and aniline scavengers in Tables 1 and 2, that of those processes yielding a radioactive molecule of the target type, ca. 34/43 i.e. 79 per cent are hot processes in the case of irradiated methylene bromide, and ca. 34/46 i.e. 74 per cent are hot processes in the case of bromoform. Of those processes yielding an active daughter molecule with one bromine atom more than the target molecule, ca. 7/17 i.e. 41 per cent are hot processes in the case of methylene bromide and ca. 13/35 i.e. 37 per cent are hot processes in the case of bromoform.

The above evidence taken together strongly suggests that primary amines can act as scavengers of radicals produced by hot atoms. As a class of scavenging substances they may prove very useful in hot atom chemistry. Halogen scavengers have the drawback in studies of the hot atom chemistry of organic halides that at the higher scavenger concentrations a hot atom may lose its identity by the process

$$X^* + X_2 \rightarrow X^*X + X$$

Furthermore, halogen scavengers are chemically very reactive in certain systems. For example, in reactor irradiations involving hundreds of rads/sec dose rates, iodine or bromine scavengers can rapidly disappear from some systems by radiation induced reactions, a drawback which would not be shared by amine scavengers.

Since the above work was completed the author became acquainted with the

Vol. 15 1960

TABLE 1.—DISTRIBUTION OF ORGANICALLY RETAINED ^{80}Br IN FRACTIONS OF IRRADIATED METHYLENE BROMIDE

1	2	3	4	5	6	7	8	9	10	11
Experiment no.	Target (MF = mole fraction)	% activity in organic phase in:				% total activity in organic phase	Av. % total activity (calc) in:			
		CH_2Br_2	$CHBr_3$	"CBr_4"	Unaccounted for		CH_2Br_2	$CHBr_3$	"CBr_4"	Unaccounted for
1	CH_2Br_2	54	19	16	11					
2	CH_2Br_2	55	23	16	6					
3	CH_2Br_2	51	20	16	13					
4	CH_2Br_2	57	20	8·6	14·4					
		54	21	14·2	10·8	79	43	17	11	9
5	CH_2Br_2 + 0·01 MF $C_6H_5NH_2$	68	10	6·9	15·1					
6	CH_2Br_2 + 0·01 MF $C_6H_5NH_2$	63	12	8·0	17·0					
7	CH_2Br_2 + 0·01 MF $C_6H_5NH_2$	66	11	9·2	13·8					
8	CH_2Br_2 + 0·01 MF $C_6H_5NH_2$	63	11	8·3	17·7					
		65	11	8·1	15·9	50	33	6	4	8
9	CH_2Br_2 + 0·01 MF Br_2	66	18	11	5					
10	CH_2Br_2 + 0·01 MF Br_2	73	13	10	4					
11	CH_2Br_2 + 0·01 MF Br_2	72	17	10	1					
12	CH_2Br_2 + 0·01 MF Br_2	64	16	10	10					
		69	16	10	5	50	35	8	5	3

TABLE 2.—DISTRIBUTION OF ORGANICALLY RETAINED ^{80}Br IN FRACTIONS OF IRRADIATED BROMOFORM

1	2	3	4	5	6	7	8	9	10	11
Experiment no.	Target (MF = mole fraction)	% activity in organic phase in:				% total activity in organic phase	Av. % total activity (calc) in:			
		CH_2Br_2	$CHBr_3$	CBr_4	Unaccounted for		CH_2Br_2	$CHBr_3$	CBr_4	Unaccounted for
13	$CHBr_3$	5·3	53	33	8·7					
14	$CHBr_3$	4·4	57	41	−2·4					
15	$CHBr_3$	3·8	47	41	8·2					
16	$CHBr_3$	4·2	53	43	−0·2					
		4·4	53	40	2·6	87	3·8	46	35	2·3
17	$CHBr_3$ + 0·01 MF $C_6H_5NH_2$	6·4	54	17	22·6					
18	$CHBr_3$ + 0·01 MF $C_6H_5NH_2$	8·8	60	15	16·2					
19	$CHBr_3$ + 0·01 MF $C_6H_5NH_2$	9·2	58	15	17·3					
20	$CHBr_3$ + 0·01 MF $C_6H_5NH_2$	9·0	63	15	13·0					
		8·4	59	16	16·6	54	4·5	32	9	9
21	$CHBr_3$ + 0·01 MF Br_2	6·8	70	37	−13·8					
22	$CHBr_3$ + 0·01 MF Br_2	5·9	59	27	8·1					
23	$CHBr_3$ + 0·01 MF Br_2	5·0	70	33	−8·0					
24	$CHBr_3$ + 0·01 MF Br_2	6·9	64	29	0·1					
		6·2	66	32	−4·2	53	3·3	35	17	−2·2

results of a gas chromatographic analysis of products of neutron irradiation of n- and isopropyl bromides with various added primary amine scavengers.[6] Once again total retention was lowered by all primary amines added, and also by some secondary amines.

Curves of retention as a function of amine concentration were not shown. However, in the case of both propyl bromides the retention in the parent molecule fell much less markedly on addition of primary amines than in the 2-bromine compound H_3C CHBr CH_2Br, in agreement with the findings in Tables 1 and 2 of the present work.

Acknowledgements—The author would like to thank Mrs. B. KOSIAK and Miss S. LASKOWSKA for skilled technical assistance.

[6] W. HERR, F. SCHMIDT and G. STOCKLIN, *Conference on Recoil Chemistry*. Institut Interuniversitaire des Sciences Nucléaires, Université de Louvain (1959).

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J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 46 to 49. Pergamon Press Ltd. Printed in Northern Ireland

SOME PROPERTIES OF THE UNSTABLE INTERMEDIATE PRODUCED BY ISOMERIC TRANSITION OR (n,γ) REACTION IN BROMATES

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(*Received* 26 *October* 1959)

Abstract—Some properties of the unstable intermediate, probably BrO_2^{2+}, formed in (n,γ) reaction and isomeric transition in bromates have been studied. The most probable reaction whereby the Br* of such a fragment comes to be present as bromate is a hydration reaction insensitive to pH, and in the case of isomeric transition, insensitive to ionic strength.

FROM previous work it appears that when isomeric transition or (n,γ) reaction occurs in bromate solutions an unstable intermediate fragment, probably BrO_2^{2+}, is produced in a significant number of events.[1,2,3] At pH 7 the Br* of such a fragment comes to be present finally as BrO_3^-. The existence of the fragment is revealed, however, by allowing the nuclear transformations to occur in the presence of methanol at mole fractions above about one in twenty, when the bromite fragment is reduced to lower valency forms.[1,2] On the basis of similar evidence the formation of an unstable iodite fragment in neutron irradiated iodate solutions has been postulated.[4]

The Br* of the intermediate fragment could be found eventually as BrO_3^- in the absence of added reductant on the basis of one of the following conceivable mechanisms:

(1) An exchange reaction between BrO_2^{2+} and BrO_3^-. The encountering of a bromate ion before complete discharge of the BrO_2 fragment would give a situation electrostatically favourable for complex formation and exchange. Such a complex would recall the complex postulated as being formed between IO_2^+ and I^-, with participation of H^+ and A^-, as an intermediate in the exchange between IO_3^- and I_2.[5]

(2) BrO_2^{2+} might discharge to BrO_2, which could then perhaps undergo an oxido-reduction with water, analogous to that observed with solutions of ClO_2,[6] giving BrO_3^- and lower valency Br.

(3) BrO_2^+ formed directly or by discharge of BrO_2^{2+} may immediately undergo the reaction

$$BrO_2^+ + H_2O \rightarrow BrO_3^- + 2H^+.$$

Neutralization of the bromite fragments might be expected to occur without their

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[1] I. G. CAMPBELL, *J. Chim. Phys.* **56**, 480 (1959).
[2] I. G. CAMPBELL, *J. Chim. Phys.* **56**, 665 (1959); Report 79/V, Polish Academy of Sciences, Institute of Nuclear Research, Warsaw (1959).
[3] G. HARBOTTLE, Brookhaven National Laboratory Report BNL 4282 (1959); *J. Amer. Chem. Soc.* **82**, 805 (1960).
[4] R. E. CLEARY, W. H. HAMILL and R. R. WILLIAMS, *J. Amer. Chem. Soc.* **74**, 4675 (1952).
[5] O. MYERS and J. KENNEDY, *J. Amer. Chem. Soc.* **72**, 897 (1950).
[6] J. W. MELLOR, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 2, pp. 288–289; Supplement 2, Part I, pp. 531, 748.

Vol. 15 1960

dissociation if transitions from potential energy curves for $BrO_2^{2+}{\cdot}H_2O$ to $BrO_2^{2-1+}{\cdot}H_2O^+$ occurred at relatively small distances of fragment-molecule separation, so that a relatively large fraction of ionization energy would appear as kinetic energy of the ion pair, rather than energy of excitation.[7] Non-dissociative neutralization of BrO_2^{2+} to BrO_2^+ can also be expected to occur because of the total energy difference of only 5·5 eV involved for electron transfer from oxygen. In addition some BrO_2^+ fragments will be formed directly as a result of the Auger cascade.

To investigate these possibilities the experiments of Table 1 were done. ^{80m}Br-labelled bromate was prepared as before, and neutron irradiations were done with a

TABLE 1.—PERCENTAGE OF ^{80}Br ACTIVITY IN LOWER VALENCY FORMS AFTER ISOMERIC TRANSITION AND (n,γ) REACTION IN BROMATES

Experiment no.	Experimental conditions	% Br in lower valency forms
	Isomeric transition	
1–8	0·14 M $NaBrO_3$, pH 7 room temp	68 ± 2·3
9–13	0·0075 M $NaBrO_3$, pH 7 room temp	67 ± 3·9
14–18	0·00375 M $NaBrO_3$, pH 7 room temp	68 ± 5·9
19–33	0·14 M $NaBrO_3$, 1·6 M $NaClO_4$, pH 7 room temp	81 ± 10
34–48	0·14 M $NaBrO_3$, 3·4 M $NaNO_3$, pH 7 room temp	82 ± 6·2
49–53	0·14 M $NaBrO_3$, 2·2 M $(NH_4)_2SO_4$, pH 7 room temp	68 ± 4·6
54–59	0·14 M $NaBrO_3$, pH 4·0, room temp	74 ± 1·9
59–64	0·14 M $NaBrO_3$, pH 3·0, room temp	74 ± 2·2
65–69	0·14 M $NaBrO_3$, pH 2·0, room temp	72 ± 4·5
69–72	0·14 M $NaBrO_3$, pH 7, 60°C	69 ± 6·3
73–78	0·14 M $NaBrO_3$, pH 7, 90°C	77 ± 3·2
79–83	NH_4BrO_3 crystals kept at room temp for 2 hours, dissolved to give ~0·14 M solution at pH 7	74 ± 7·5
	$^{79}Br(n,\gamma)^{80}Br$ reaction	
84–89	1·8 M $NaBrO_3$, pH 7·0 irradiated	90 ± 3·2
90–95	1·8 M $NaBrO_3$, 1·6 M $NaClO_4$, pH 7, irradiated	90 ± 1·3
96–102	$NaBrO_3$ crystals irradiated, dissolved in 1·6 M $NaClO_4$, pH 7	89 ± 1·8
103–110	$NaBrO_3$ crystals irradiated, dissolved in water pH brought to 7	81 ± 1·5

500 mg Ra/Be source as previously described.[1,2] In all cases lower valency forms were separated on a preformed AgBr precipitate by the method already given. Small corrections were applied for lower valency activity not separated on a single precipitate using average values of coefficients of separation. These were measured in the given conditions of solution with carrier-free solutions of lower valency ^{80}Br prepared by Szilard–Chalmers reaction from irradiated bromoform, as already described. These experiments also served to check the absence of exchange between lower valency forms and bromate in the given conditions.

Mechanism 1 might be expected to show a dependence of the bromate retention after isomeric transition on the bromate concentration of the solution, if it were

[7] J. L. MAGEE and E. F. GURNEE, *J. Chem. Phys.* **20**, 894 (1952).

competing with a reaction of oxidation of water by the BrO_2 fragment leading to formation of lower valency Br. Experiments 1–18 of Table 1, together with experiments 9–13 of the previous series[1] show that retention does not vary significantly in the range of bromate concentration from 0·00375 M to 1·2 M.

Mechanism 1 could also be expected to show a marked dependence of retention on pH. The relative yield of BrO_3^- and lower valency Br formed by reactions of BrO_2 in mechanism 2 can also be expected to be dependent on pH.[6] On the other hand despite the formation of H^+ in mechanism 3, equilibrium probably lies so far to the right that this reaction could be insensitive to pH. Experiments 54–69 of Table 1 show only a very slight and statistically doubtful lowering of bromate retention by comparison with experiments 1–8. These results together with experiments 26–32 of the previous series,[1] show that bromate retention in solution is only slightly if at all dependent on pH in the range 2–12. Incidentally it is interesting that experiments with carrier-free solutions of lower valency Br* from Szilard–Chalmers reaction showed only a very small exchange into bromate after 2 hr at pH 2, a necessary pre-condition for success of experiments 65–69.

Mechanisms 1 and 2 might perhaps be expected to lead to a dependence of bromate retention on temperature. Experiments 69–78 in Table 1 were done to check this point. Retention drops from 32 (in experiments 1–8) to 23 as temperature is raised from ambient to 90°C. A drop in retention does not directly support mechanisms 1 and 2, but seems to indicate that a process competing with those leading to bromate retention and leading to bromite reduction, say oxidation of water, has been accentuated by the rise in temperature.

Mechanism 1 might be expected to be sensitive to the ionic strength of the medium. As the ionic strength is increased the potential of the BrO_2^{z+} and BrO_3^- ions should fall, creating a situation less favourable for complex formation. In addition, if a complex of the type $BrO_2^+ A^- BrO_3^- C^+$ were involved similar to the intermediate in the $IO_3^- \leftrightharpoons I_2$ exchange,[5] one might expect a dependence on the ionic strength of the medium. It has also been pointed out that charge transfer in such complexes would require an eventual redistribution of surrounding ions, giving an electrolyte effect.[8] The evidence of experiments 19–53 is somewhat equivocal. Retention is unchanged when the solution is made 2·2 M in $(NH_4)_2 SO_4$. The apparently marked reductions of retention in the presence of $NaClO_4$ or $NaNO_3$ are not statistically significant because of the large error obtained despite the relatively large number of experiments. Experiments with carrier-free solutions of lower valency ^{80}Br showed that these errors did not arise from a capriciousness of the AgBr separation method in these conditions, but that the scatter in the results reflects a real criticality in the system with respect to unknown factors.

To summarize the above evidence, the finding that retention is independent of bromate concentration and pH supports mechanism 3 rather than mechanism 1 or 2, the evidence from experiments with added electrolyte being inconclusive.

Experiments 79–83 show that the bromate retention is the same when isomeric transition occurs in NH_4BrO_3 crystals as when it occurs in $KBrO_3$ crystals (experiments 129–134 of ref. 2). This indicates that the ammonium ion in the crystal cannot reduce the BrO_2^{z+} fragment before dissolution of the crystal. Such a reduction by

[8] H. TAUBE, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 1, p. 1 (1959).
[5] G. HARBOTTLE and N. SUTIN, *Advances in Inorganic Chemistry and Radiochemistry* Vol. 1, p. 267 (1959).

Vol. 15 1960

NH_4^+ has been evoked to explain lowered retentions in ammonium salts in comparison with potassium and sodium salts in the case of (n,γ) reactions.[9] The lack of influence of NH_4^+ on the retention in the present experiments supports the author's previous conclusion that in the case of isomeric transition in crystalline bromates negligable separation of the fragments leads to immediate recombination in the case of BrO_2^{z+} and thus to the found insensitivity to thermal annealing or subsequent dissolution of the crystal in methanol solutions.[2] HARBOTTLE has recently given evidence, however, which suggests that separation of all fragments is not negligeable in the case of this isomeric transition.[3] Unfortunately the liability of NH_4BrO_3 to detonate precludes the possibility of comparing the isomeric transition results with those of the (n,γ) reaction.

Experiments 84–95 lead to the conclusion that the ionic strength of the solution does not influence the behaviour of the bromite fragment formed in (n,γ) reaction in solution. Experiments 96–110 seem to show definitely that when crystals are irradiated and dissolved in 1·6 M $NaClO_4$ the retention is only approximately half that observed when the crystals are dissolved in water. This result suggests recourse to mechanism I, sensitive to electrolytic strength, but the result is not at present understood by comparison with the results for the isomeric transition or with the previously obtained evidence which seemed to suggest that BrO_2 fragments are completely recombined in the crystal before dissolution.[2]

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J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 50 to 62. Pergamon Press Ltd. Printed in Northern Ireland

CHARGE-TRANSFER SPECTRA IN METAL COMPLEXES, ESPECIALLY IN HALOGENOPENTAMMINECOBALT(III) IONS*

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Abstract—A theory has been developed to interpret the intense absorption bands (believed to be charge-transfer bands) in the ultra-violet of halogenopentamminecobalt(III) spectra. The theory is based on the LCAO MO theory and includes consideration of spin–orbit interaction, which is proved to be important especially with the bromo- and iodo-complexes. Quantitative prediction of intensity ratios for each pair of the bands and semiquantitative calculation of the intensity of each band are made and satisfactorily compared with observation. In the course of this calculation, suggestions are made for mixing of orbitals and for delocalization of the charge transfer. The bond energy of the complex is discussed in connexion with the wave numbers of the bands. A general opinion is expressed that the spectra of many metal complexes can to a first approximation be interpreted with the LCAO MO model.

Vol.
15
1960

TRANSITION-METAL compounds are known to have characteristic colours, due to absorption bands in the near-infra-red, visible, and near-ultra-violet region of the spectra. The absorption bands may be classified into two categories, the weaker and the stronger ones with molar extinction coefficients of the order of 10^2 or less and of the order of 10^3–10^5, respectively. Taking cobalt(III) complexes as an illustration, the nature of the weak bands has been discussed in detail in previous papers,[1] and now in this paper the nature of the intense bands will be considered.

It has been known for many years that the chloro-, bromo-, and iodo-pentammine-cobalt(III) ions have two intense bands in the ultra-violet of the spectra. These bands are named differently by different investigators: "the third and fourth bands" by LINHARD and WEIGEL[2], "the specific and third bands" by YAMADA and co-workers including TSUCHIDA[3], "the first and second charge-transfer bands" by ORGEL[4], and "the IIIa and IIIb bands" by NAKAMOTO and co-workers including TSUCHIDA[5]. As will be seen later, the bands at the highest wave-numbers may correspond to the third band of the hexamminecobalt(III) spectrum, and therefore the names given by YAMADA *et al.* and by NAKAMOTO *et al.* may be logical, but the names given by LINHARD and WEIGEL, the third and fourth bands, will be used in this paper for the sake of simplicity.

* Briefly communicated in *Naturwissenschaften* **44**, 632 (1957).

[1] H. YAMATERA, *J. Inst. Polytech. Osaka City Univ.* **5**, Series C, 163 (1956); *Naturwissenschaften* **44**, 375 (1957); *Bull. Chem. Soc. Japan* **31**, 95 (1958).
[2] M. LINHARD and M. WEIGEL, *Z. Anorg. Chem.* **266**, 49 (1951); **271**, 101 (1952); *Neue Folge* **5**, 20 (1955).
[3] S. YAMADA, A. NAKAHARA, Y. SHIMURA and R. TSUCHIDA, *Bull. Chem. Soc. Japan* **28**, 222 (1955).
[4] L. E. ORGEL, The 10th Solvey Conference (1956).
[5] K. NAKAMOTO, J. FUJITA, M. KOBAYASHI and R. TSUCHIDA, *J. Chem. Phys.* **27**, 439 (1957).

Intense absorption bands in metal complexes may in general arise from

(i) allowed electronic transitions in the central metal ion, such as $(n-1)d \rightarrow np$,

(ii) allowed electronic transitions in the ligands, or

(iii) charge-transfer transitions from the ligands to the metal or vice versa.

With halogenoamminecobalt(III) complexes, the second will not be the case since the ligands have no such transitions near the wave-number regions under consideration and with these complexes the charge transfer must occur from the ligands to the metal since ligands have no low-lying vacant orbital that can accept the electron from the metal. Before entering detailed discussion of the problem, a brief review of theories concerning the absorption bands in question will be given in the following paragraphs.

LINHARD and WEIGEL[2] made a systematic study of these halogenoamminecobalt (III) and related series of complexes, and attributed the intense bands to the charge transfer within the complex from the halide ion to the cobalt(III) ion. They suggested that the appearance of the bands in pair would probably be connected with the ground and an excited state, for example the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states, of the halogen atom in the excited complex, or, alternatively, related to the two states of the resulting cobalt(II) ion in the complex. ORGEL[4] assigned the third band to the almost completely charge-transfer transition from a halogen orbital to the metal d_{z^2} orbital and the fourth band to a less completely charge-transfer transition from the bonding orbital of the cobalt–halogen bond to the metal d_{z^2} orbital. This assignment may belong to the first alternative suggested by LINHARD and WEIGEL. On the other hand, NAKAMOTO *et al.*[5] have made a semi-empirical calculation to interpret the spectra of chloroammines of cobalt(III), and have come to the conclusion that the third and fourth bands are attributable to transitions of chlorine electrons to slightly antibonding and strongly antibonding orbitals derived from cobalt 3*d* orbitals (d_{z^2} and $d_{x^2-y^2}$), a conclusion which may be classified into the second alternative according to LINHARD and WEIGEL. Recently, JØRGENSEN[6] reported that the interpretation of ORGEL[4] and YAMATERA[7] is one of the two possibilities, but he prefers the other type of interpretation that the two bands both are due to the transfer of a π-electron.

Some authors including LIEHR and BALLHAUSEN[8] and BASOLO and PEARSON[9] seem to be of the opinion that the intense absorption at about 2000 Å is partly due to a $d \rightarrow p$ transition, which may essentially be the $3d \rightarrow 4p$ transition in the central cobalt. Thus they considered that the energy difference between the 3*d* and 4*p* of the cobalt ion decreased through complex formation. However, in view of the very large energy difference between the levels in the free ion that may amount to more than twice the energy of the absorption and on account of the probable antibonding character of the 4*p* orbital, it seems unlikely that the 4*p* level comes so near to the 3*d* level as to be consistent with the wave-numbers of the absorption.* So in this paper the absorption is considered to be connected with the charge transfer. (This does not mean to exclude the possibility that the orbital to which the charge transfer passes may to some extent have the character of the cobalt 4*p* orbital.)

* Although the occupied d_{yz} and d_{zx} orbitals are somewhat antibonding due to π interaction with the halogen $p\pi$-orbitals, the energy increase of the d_{yz} (d_{zx}) level cannot be great enough to account for the wave-numbers of the absorption.

[6] C. K. JØRGENSEN, *Absorption Spectra of Complexes of Heavy-Metals* (1958).

[7] H. YAMATERA, *Naturwissenschaften* **44**, 632 (1957).

[8] A. D. LIEHR and C. J. BALLHAUSEN, *Phys. Rev.* **106**, 1161 (1957).

[9] F. BASOLO and R. G. PEARSON, *Mechanism of Inorganic Reactions* p. 84. John Wiley, New York (1958).

Among the interpretations that are based on the charge transfer, the one that was suggested by LINHARD and WEIGEL and that relates the two bands to the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states of the halogen atom cannot be justified at least for the chloropentammine-cobalt(III) case, since the separation of the two bands is very much greater than the energy difference between the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states. (Again this does not mean that there is no spin–orbit interaction. As will be seen, the spin–orbit interaction actually exists.) The other possible interpretations mentioned above are summarized in Table 1, together with the calculated moment of each transition for the chloro-pentamminecobalt(III).

TABLE 1.—VARIOUS ASSIGNMENTS OF THE CHARGE-TRANSFER BANDS

Transition	Calculated transition† moment (and its direction) (a.u.)	Assignment*			
		O	N	J	Y
$p\pi \rightarrow d_{z^2}$ producing					
singlet state	0·05 (x, y)	III	III	IV	III
triplet state	0·1 (z)	—	—	III	III
$p\sigma \rightarrow d_{z^2}$	1–2 (z)	IV	III	—	IV
$p\pi \rightarrow d_{x^2-y^2}$	0·02 (x, y)	—	IV	—	—
$p\sigma \rightarrow d_{x^2-y^2}$	0	—	IV	—	—

Observed values: III, ~0·2 (x, y and z); IV, ~1·3. The calculated and observed values are those for $[Co(NH_3)_5Cl]^{2+}$.

* O = ORGEL[4]; N = NAKAMOTO *et al.*[5]; J = JØRGENSEN[6]; Y = YAMATERA[7] and present paper.
† See Appendix 1.

Vol. 15 1960

It may be seen from Table 1 that ORGEL–YAMATERA's interpretation would be the most probable, although the calculated intensity of the third band is much lower than the observed. A more certain conclusion will be drawn from the following molecular-orbital treatment of the problem where spin–orbit interaction is also taken into account.

THEORY

There seems to be little doubt that the intense bands result from charge-transfer transitions from the halogen to the cobalt. Of the two low-lying unoccupied orbitals of the cobalt, $d_{x^2-y^2}$ lies along four Co—N bonds and only slightly overlaps the region where a halogen electron exists in appreciable probability, and accordingly a transition to $d_{x^2-y^2}$ will so rarely occur that the corresponding absorption band does not seem to be very strong compared with the first and second bands (see Table 1). On the other hand, d_{z^2} lies along the Co—X axis and a transition to this orbital may produce a strong absorption. Thus consideration of the cobalt d_{z^2} and the chlorine orbitals will be sufficient for the present problem.

Then the complex may be regarded as a linear molecule, since the ammonia ligands off the Co—X axis neither directly participate in the transition under consideration nor affect the σ and π characters of the orbitals to be considered.

Table 2 is a list of the excited states that may be produced by charge-transfer transitions from the halogen orbitals to the cobalt d_{z^2}. In the first column are given arbitrary notations of the states, in the second the notations according to the (J_1, J_2)

coupling case,[10] in the third the (Λ, S) coupling notations[10] of the corresponding states, and in the fourth the zeroth-order wave functions; the notation $\psi(p_{-1}^{-} \rightarrow d_0^{+})$, for example, represents the wave function of the excited state that will be produced if a halogen p electron with $m = -1$ and $m_s = -\frac{1}{2}$ is moved to the cobalt d_{z^2} orbital (where $m = 0$) accompanied by change of the spin to $m_s = \frac{1}{2}$. Treatment has been made on the assumption of the (J_1, J_2) coupling, which was proved, at least in the cases of the iodo- and bromo-complexes, to be a better approximation than the (Λ, S) coupling.

TABLE 2.—EXCITED STATES OF $[Co(NH_3)_5X]^{2+}$ PRODUCED BY CHARGE TRANSFER FROM THE HALOGEN ORBITAL TO THE COBALT d_{z^2}.

State	$\Omega(J_1, J_2)$	Corresponding (Λ, S) state (mixed with)	0-order wave function*
B	0^+	$^1\Sigma_0^+$ (b $^3\Pi_{0^+}$)	$\psi_B^0 = (1/\sqrt{2})\{\psi(p_0^+ \rightarrow d_0^+) + \psi(p_0^- \rightarrow d_0^-)\}$
A	1	$^1\Pi_1$ ($^3\Sigma_{\pm 1}^+$)	$\psi_A^0 = (1/\sqrt{2})\{\psi(p_{\pm 1}^+ \rightarrow d_0^+) + \psi(p_{\pm 1}^- \rightarrow d_0^-)\}$
f	1	$^3\Sigma_{\pm 1}^+$ ($^1\Pi_1$)	$\psi_f^0 = \psi(p_0^- \rightarrow d_0^+)$, $\psi(p_0^+ \rightarrow d_0^-)$
e	0^-	$^3\Sigma_0^+$ (a $^3\Pi_{0^-}$)	$\psi_e^0 = (1/\sqrt{2})\{\psi(p_0^+ \rightarrow d_0^+) - \psi(p_0^- \rightarrow d_0^-)\}$
d	2	$^3\Pi_{0^-}$	$\psi_d^0 = (1/\sqrt{2})\{\psi(p_{-1}^- \rightarrow d_0^+) \pm \psi(p_1^+ \rightarrow d_0^-)\}$
c	1	$^3\Pi_1$ ($^3\Sigma_{\pm 1}^+$)	$\psi_c^0 = (1/\sqrt{2})\{\psi(p_{\pm 1}^+ \rightarrow d_0^+) - \psi(p_{\pm 1}^- \rightarrow d_0^-)\}$
b	0^+	$^3\Pi_{0^+}$ (B $^1\Sigma_0^+$)	$\psi_b^0 = (1/\sqrt{2})\{\psi(p_1^- \rightarrow d_0^+) + \psi(p_{-1}^+ \rightarrow d_0^-)\}$
a	0^-	$^3\Pi_{0^-}$ ($^3\Sigma_0^+$)	$\psi_a^0 = (1/\sqrt{2})\{\psi(p_1^- \rightarrow d_0^+) - \psi(p_{-1}^+ \rightarrow d_0^-)\}$
X	0^+	$^1\Sigma_0^+$	Ground state

* See Appendix 2.

There may be three possibilities in the choice of the coupling scheme: (Λ, S) coupling, (J_1, J_2) coupling, and (Ω_c, ω) coupling.[10] In Table 2a are given various quantum numbers concerning angular momenta of the system for the wave functions under consideration. In the table, ψ_X represents the wave function of the ground state. J_1 and J_2 are quantum numbers of the total angular momentum of the chlorine and the cobalt electrons, respectively. If all the chlorine electrons are considered to be core electrons and the odd electron of the cobalt is considered to be an outer electron, $\Omega_c = M_{J_1}$ and $\omega = M_{J_2}$ and therefore (J_1, J_2) coupling is equivalent to (Ω_c, ω) coupling.

An important difference between the (J_1, J_2) and (Λ, S) coupling cases is as follows. In the (J_1, J_2) case, $\psi(p_1^- \rightarrow d_0^+)$ has the total quantum number zero and will be mixed with $\psi(p_{-1}^+ \rightarrow d_0^-)$ to result in the b state, whereas in the (Λ, S) case $\psi(p_1^+ \rightarrow d_0^-)$ is such a function. There is spin–orbit interaction between $\psi(p_1^- \rightarrow d_0^+)$ and $\psi(p_0^+ \rightarrow d_0^+)$, a constituent function of the B state, but no such interaction between $\psi(p_1^+ \rightarrow d_0^-)$ and $\psi(p_0^+ \rightarrow d_0^+)$. Accordingly the spin–orbit interaction between the B and b states is twice as great for the (J_1, J_2) coupling case as for the (Λ, S) case, since the other constituent functions of the b and B states are the same for both cases and have spin–orbit interaction with each other.

Choice of the coupling scheme may be made through comparison in magnitude of the spin–orbit interaction in the halogen atom and the exchange interaction of the unpaired electrons. As regards the $\psi(p_0 \rightarrow d_0)$ states, treatment according to either coupling scheme will lead to the same result, and therefore only the $\psi(p_{\pm 1} \rightarrow d_0)$ states are to be considered. The exchange integral of the halogen p_1 orbital and the cobalt d_0 orbital (mixed with the halogen p_0 orbital) $K(p_{\pm 1}, d_0)$, which is half the energy difference between the singlet and triplet states, may be evaluated as follows:

$$K(p_1, d_0) = c_1^2 K(p_1, d_0^{+}) + c_2^2 K(p_1, p_0^{-}) \simeq c_2^2 K(p_1, p_0^{-})$$
$$= c_2^2 \times 3F_2 = (0{\cdot}1 \sim 0{\cdot}3) \times 3 \times (1700 \sim 1800) \simeq 1 \times 10^3,$$

[10] G. HERZBERG, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* pp. 319, 216. Van Nostrand, New York (1950).

where d_0^+ and p_0^+ represent the purely cobalt and halogen orbitals which are mixed to form the d_0 orbital in the manner,

$$d_0 = c_1 d_0^+ - c_2 p_0^+$$

F_2 is the Slater-Condon parameter in the halogen atom, the estimated value being that for chlorine. The magnitude of the exchange integral seems to be the same order also for the other halogens.

On the other hand the spin–orbit interaction differs substantially for different halogens. Thus the energy difference between the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states of a halogen atom varies from 880 cm^{-1} for chlorine to 3700 cm^{-1} for bromine and 7500 cm^{-1} for iodine.

TABLE 2a.—ANGULAR-MOMENTUM QUANTUM NUMBERS OF THE WAVE FUNCTIONS

Wave function	Λ	Σ	M_{J_1}	M_{J_2}	$\Omega_{(\Lambda,S)}$	$\Omega_{(J_1,J_2)} = \Omega_{(\Omega_e,\omega)}$
ψ_Σ	0	0	0	0	0	0
$\psi(p_0^+ \rightarrow d_0^+)$	0	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	0
$\psi(p_0^- \rightarrow d_0^+)$	0	1	$\frac{1}{2}$	$\frac{1}{2}$	1	1
$\psi(p_0^+ \rightarrow d_0^-)$	0	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	1
$\psi(p_0^- \rightarrow d_0^-)$	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	0
$\psi(p_1^+ \rightarrow d_0^+)$	1	0	$-\frac{3}{2}$	$\frac{1}{2}$	1	1
$\psi(p_1^- \rightarrow d_0^+)$	1	1	$-\frac{1}{2}$	$\frac{1}{2}$	2	0
$\psi(p_{-1}^+ \rightarrow d_0^+)$	1	0	$\frac{1}{2}$	$\frac{1}{2}$	1	1
$\psi(p_{-1}^- \rightarrow d_0^-)$	1	1	$\frac{3}{2}$	$\frac{1}{2}$	2	2
$\psi(p_1^+ \rightarrow d_0^-)$	1	−1	$-\frac{3}{2}$	$-\frac{1}{2}$	0	2
$\psi(p_1^- \rightarrow d_0^-)$	1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	1	1
$\psi(p_{-1}^+ \rightarrow d_0^-)$	1	−1	$\frac{1}{2}$	$-\frac{1}{2}$	0	0
$\psi(p_{-1}^- \rightarrow d_0^-)$	1	0	$\frac{3}{2}$	$-\frac{1}{2}$	1	1

From these values it may be said that in the chloro-complex the exchange interaction of the unpaired electrons in the excited states of the complex is of the same order of magnitude as, or slightly greater than, the spin–orbit interaction, whereas with the bromo- and iodo- complexes the exchange interaction is not so important as the spin–orbit interaction.

In spite of this conclusion the (J_1, J_2) coupling scheme was applied even to the chloro- case, since there was such difficulty in applying the (Λ, S) coupling scheme that no empirical (Λ, S) coupling constant was available. The error due to this less satisfactory approximation does not seem to exceed a factor of two in the problem of absorption intensity.

According to the selection rule, transition is allowed from the ground 0^+ states of the complex only to the 0^+ and 1 states, and transitions to the 1 states, however, are not expected to cause strong absorptions. Hence the b and B states will be considered first. Approximate wave functions for these states may be obtained by solving the secular equation

$$\begin{vmatrix} E_b^0 - E & \zeta/\sqrt{2} \\ \zeta/\sqrt{2} & E_B^0 - E \end{vmatrix} = 0,$$

where E_b^0 and E_B^0 are the energies of the zero-order states corresponding to ψ_b^0 and ψ_B^0, and ζ is the (L, S) coupling constant in the halogen atom; ζ is equal to $\frac{2}{3}$ of the energy separation between the states $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ of the halogen atom. The solutions of the equation will be obtained in the form

$$\psi_b = \alpha\psi_b^0 + \beta\psi_B^0$$
$$\psi_B = \alpha\psi_B^0 - \beta\psi_b^0,$$

where the coefficient α and β can be empirically determined as follows.

Vol. 15 1960

The two intense bands observed would most probably correspond to the transitions to the *b* and *B* states for the reason given above, as well as for the reasons to be given later. Then the α and β values can be calculated by putting the roots of the secular equation to the wave-numbers at the absorption maxima. The values of α^2 and β^2 thus obtained for each complex are given in Table 3.

TABLE 3.—ESTIMATED VALUES OF α^2 AND β^2

Complex	α^2	β^2
$[Co(NH_3)_5Cl]^{2+}$	0·997	0·003
$[Co(NH_3)_5Br]^{2+}$	0·945	0·055
$[Co(NH_3)_5I]^{2+}$	0·791	0·209

DISCUSSION

Ratio of intensities for the two charge-transfer bands. The ratio can easily be found from the wave functions. The zeroth-order state ψ_b^0 corresponds to a triplet states and ψ_B^0 to a singlet, and electronic transition from the ground singlet will be allowed to ψ_B^0 but not to ψ_b^0. Hence the ratio of squares of moments for the transitions $b \leftarrow X$ and $B \leftarrow X$, which is not very much different from the ratio of absorption intensities, is given by β^2/α^2. The calculated values are compared with the observed ones in Table 4. The agreement appears to be satisfactory for the bromo- and iodo-complexes, but in the case of the chloro- complex, the observed intensity ratio is about ten times greater than the calculated one. This disagreement seems to have arisen

TABLE 4.—THE RATIO OF SQUARES OF MOMENTS FOR THE TRANSITIONS $b \leftarrow X$ and $B \leftarrow X$

Complex	Intensity ratio $\frac{f_{III}}{f_{IV}}$ (obs.)	Ratio of squared transition moments $\frac{f_{III}/\nu_{III}}{f_{IV}/\nu_{IV}}$ (obs.)	$\frac{\beta^2}{\alpha^2}$ (calc.)
$[Co(NH_3)_5Cl]^{2+}$	0·022*	0·027	0·003
$[Co(NH_3)_5Br]^{2+}$	0·044*	0·054	0·058
$[Co(NH_3)_5I]^{2+}$	0·19	0·25	0·26

* The values of $\varepsilon_{III}/\varepsilon_{IV}$ are given as approximate f_{III}/f_{IV} values.
f_{III}, f_{IV}: Oscillator strength of the third and fourth bands.
ν_{III}, ν_{IV}: Wave-numbers of the third and fourth bands.
ε_{III}, ε_{IV}: Extinction coefficient at absorption maxima of the third and fourth bands.

from neglect of the transition $A \leftarrow X$, which would be more important than $b \leftarrow X$ of low transition probability in the chloro-case. In this connexion a closer consideration will be made in the following paragraphs.

Intensities of the third band. In the preceding paragraphs, the weakly allowed transitions to the 1 states have been disregarded. Of the states belonging to the 1, the *A* state approximately corresponds to a singlet state produced by the electronic transition from the chlorine π to the cobalt d_{z^2}, and the transition to this state will take place with moderate absorption; the other 1 states approximately correspond to triplet states, and transitions to these states will be negligible. The third band is then expected to consist of two sub-bands: the one related to $A \leftarrow X$ and the other

related to $b \leftarrow X$, the latter being to a first approximation the $\pi \rightarrow d_{z^2}$ transition with change of the spin.

From the observed intensity and position of the band, the total of the squared transition moment is calculated to be 0·09 a.u. (atomic unit) for the chloropentamminecobalt(III) ion, whereas according to the preceding discussion the squared moment for the $b \leftarrow X$ transition is expected to be about 0·01 a.u. A calculation will be made to see if the residual part of the squared moment is attributable to the $A \leftarrow X$ transition. With an assumption that p_1 and d_0 are the purely chlorine and the purely cobalt orbital, the moment for the transition $p_1 \rightarrow d_0$ is calculated to be about 0·05 a.u. (when squared, 0·0025 a.u.), too much lower than might be expected. But with an assumption that d_0 is not a purely cobalt orbital but is mixed with the chlorine σ orbital, which in turn is a hybrid of p and s, the transition $p_1 \rightarrow d_0$ may have some character of the strongly allowed $p_1 \rightarrow s$ transition in the chlorine; and thus the chlorine s character of d_0 that amounts to about 2 per cent will be able to account for the observed intensity of the band.* Similar reasoning may be applied to the cases of the bromo- and iodo-complexes. However, the relative importance of $A \leftarrow X$ decreases in going from the chloro- to the iodo-complex, i.e., $b \leftarrow X$ and $A \leftarrow X$ are nearly equally important in the bromo- case while $b \leftarrow X$ is the much more important one in the iodo-case.

YAMADA *et al.*[3] have made a study on dichroism of the crystal of the complex salt $[Co\ en_2Br_2]Br \cdot HBr \cdot 2H_2O$. The third band (the specific band according to their nomenclature) was observed at slightly different positions with lights polarized in different directions: in the a and b directions, which presumably did not greatly deviate from the z direction (the Br-Co-Br direction), and from the x or y direction respectively. The wave-numbers were somewhat lower and the intensity was slightly higher for the a-absorption than for the b-absorption. Assignment of the a- and b-absorptions to the transitions $b \leftarrow X$ and $A \leftarrow X$, respectively, will be consistent with the following requirements from theoretical considerations: the $b \leftarrow X$ transition (the $0^+ - 0^+$ transition) must be caused by absorption of the z-polarized light, and the $A \leftarrow X$ transition (the $1\text{–}0^+$ transition) must be polarized in the x and y directions. The b state must be lower in energy than the A state according to the general rule that a triplet state lies below the corresponding singlet.

A slight contradiction to the discussion here may be found in the aforementioned result (Table 4) concerning the ratio of intensities for the two absorption bands. In spite of disregard of the $A \leftarrow X$ transition, the observed and calculated ratios were in good agreement for the bromo- and iodo-complexes, and accordingly closer consideration would lead to a slightly poorer agreement. This contradiction may be partly due to difficulty in estimating the intensity of the third band, which appreciably overlaps the fourth band, and may be partly owing to slightly too high a value chosen as the spin-orbit coupling constant. The coupling constant for the atom was used, but in the molecule the coupling constant should be slightly lower.

Intensity of the fourth band. According to the preceding arguments, the fourth band would be due to the $B \leftarrow X$ transition, which very approximately corresponds

* This is qualitatively equivalent to saying that the observed intensity may be accounted for, if the cobalt d_0 orbital extends to the neighbourhood of the chlorine nucleus and has a charge distribution unsymmetrical with respect to the chlorine nucleus in its vicinity.

An additional reason for the high intensity of the band may be the mixing of the chlorine $p_{\pm 1}$ orbital with the cobalt $4p$.

Vol. 15 1960

to the $p_0 \rightarrow d_0$ transition in the case of the chloro-complex. The transition moments were calculated under each of the following assumptions: (i) both the bonding (essentially chlorine) and the antibonding (essentially cobalt) orbitals are localized around the cobalt-chlorine bond; (ii) the bonding orbital is localized, but the antibonding orbital is not localized around the bond, i.e., the latter is derived not from the d^2sp^3 hybridized orbital but from the d_{z^2} orbital of the cobalt (this case was hereinafter be called "partly localized"); and (iii) both the bonding and antibonding orbitals are delocalized according to the symmetry requirement of the complex (regarded as octahedral). For numerical calculation, overlap of the pure cobalt and the pure chlorine orbital (in the localized case), or of the pure cobalt orbital and the group orbital of the ligands (in the delocalized case), is assumed to be 0·3, their mixing ratios 25 : 75 and 75 : 25 for the bonding and antibonding orbitals, and the moment for transition between the 3*d* and 4*p* orbitals of the cobalt 0·2 a.u. These assumed values may not be quite satisfactory, but will be sufficient for qualitative discussion since, even if they cause considerable errors, the errors will be more or less similar in all the cases.

The wave functions used in the calculation are as follows:

(i) localized case,

$$\phi_1 = a_1\sigma_z^{\circ} + b_1\sigma_0^{\circ}$$

$$\phi_1^* = a_1^*\sigma_0^{\circ} - b_1^*\sigma_z^{\circ}$$

(ii) partly localized case,

$$\phi_1 \text{ and } \phi_2^*$$

(iii) delocalized case,

$$\phi_2 = a_2(\sigma_z^{\circ} - \sigma_{\bar{z}}^{\circ}) + b_2 p_z^{\circ}$$

$$\phi_2^* = a_2^* d_{z^2}^{\circ} - b_2^*(\sigma_z^{\circ} + \sigma_{\bar{z}}^{\circ}) + c_2^*(\sigma_x^{\circ} + \sigma_{\bar{x}}^{\circ} + \sigma_y^{\circ} + \sigma_{\bar{y}}^{\circ})$$

where ϕ_1 and ϕ_2 represent bonding orbitals and ϕ_1^* and ϕ_2^* antibonding orbitals; σ_z°, $\sigma_{\bar{z}}^{\circ}$, etc., the σ orbitals of the ligands on the axes z, $-z$, etc.; $d_{z^2}^{\circ}$ and p_z° the cobalt $3d_{z^2}$ and $4p_z$ orbitals; and σ_0° one of the hybridized d^2sp^3 orbitals in the z direction. The superscript $\circ$ means that the orbital is a purely cobalt or chlorine orbital. The parameter values are assumed as follows: $a_1 = 0{\cdot}81$, $b_1 = 0{\cdot}39$, $a_1^* = 0{\cdot}97$, $b_1^* = 0{\cdot}67$, $a_2 = 0{\cdot}81/\sqrt{2} = 0{\cdot}57$, $b_2 = 0{\cdot}39$, $a_2^* = 0{\cdot}97$, and $b_2^* = 0{\cdot}67\sqrt{3} = 0{\cdot}39$, the parameter c_2^* being of little importance in the calculation. These values are consistent with the assumption mentioned in the text as well as with a simplified model of the system in which all the ligand σ orbitals mix with cobalt orbitals to the same extent, and in which the cobalt 3*d*, 4*s* and 4*p* orbitals have the same radial distribution of the electrons and differ only in the angular distribution.

The calculation of the moment for the $\phi_1 \rightarrow \phi_1^*$ electron jump (in case (i)) is:

$$\begin{aligned}(\phi_1|ez|\phi_1^*) &= e[b_1a_1^*(\sigma_0^{\circ}|z|\sigma_0^{\circ}) - a_1b_1^*(\sigma_z^{\circ}|z|\sigma_z^{\circ}) + \\ &\quad + (a_1a_1^* - b_1b_1^*)(\sigma_0^{\circ}|z|\sigma_z^{\circ})] \\ &= e[b_1a_1^*\{(\sigma_0^{\circ}|z|\sigma_0^{\circ}) - (\sigma_z^{\circ}|z|\sigma_z^{\circ})\} + \\ &\quad + (a_1a_1^* - b_1b_1^*)\{(\sigma_0^{\circ}|z|\sigma_z^{\circ}) - S(\sigma_z^{\circ}|z|\sigma_z^{\circ})\}] \\ &\cong e[b_1a_1^*(r_0 - r_z) + (a_1a_1^* - b_1b_1^*)S(r_{0z} - r_z)]\end{aligned}$$

where S represents the overlap integral of the orbitals; r_0, r_z, and r_{0z} represent the average positions (the z co-ordinates) of the σ_0° and σ_z° orbitals and of where the two orbitals overlap, respectively. With $r_z = 4{\cdot}4$ (equal to the position of the chlorine nucleus), $r_{0z} = 2{\cdot}4$, $r_0 = 1{\cdot}2$ (the last two being chosen in consideration of the classical radius of the orbitals but rather arbitrarily), and $S = 0{\cdot}3$, the moment $(\phi_1|ez|\phi_1^*)$ was calculated to be about 1·5, and consequently the totals of the squared transition moments for the band are $2 \times 1{\cdot}5^2$ in the monochloro- and $4 \times 1{\cdot}5^2$ in the *trans*-dichloro-case.

In case (iii)

$$\begin{aligned}(\phi_z|ez|\phi_z^*) = [&ea_z a_z^*\{(\sigma_z^\circ|z|d_{z^2}^\circ) - (\sigma_{\bar{z}}^\circ|z|d_{z^2}^{\bar{z}})\} - \\ &-a_z b_z^*\{(\sigma_z^\circ|z|\sigma_z^\circ) - (\sigma_z^\circ|z|\sigma_{\bar{z}}^{\bar{z}})\} + \\ &+b_z a_z^*(p_z^\circ|z|d_{z^2}^\circ) - \\ &-b_z b_z^*\{(p_z^\circ|z|\sigma_z^\circ) + (p_z^\circ|z|\sigma^{-\circ})\}] + \\ &+ \text{neglected terms} \\ \simeq\ & e[a_z a_z^* S_d(r_{0z} - r_{0\bar{z}}) \\ &-a_z b_z^*(r_z - r_{\bar{z}}) + \\ &+b_z a_z^*(p_z^\circ|z|d_{z^2}^{\bar{z}}) - \\ &-b_z b_z^* S_p\{r_{0z} + (-r_{0\bar{z}})\}]\end{aligned}$$

where S_d and S_p represent overlap integrals of the σ_z° or $\sigma_{\bar{z}}^{\bar{z}}$ orbital and respectively the cobalt d_{z^2} and p_z° orbitals. With $S_d = 0{\cdot}3/\sqrt{3} = 0{\cdot}17$, $S_p = 0{\cdot}3/\sqrt{2} = 0{\cdot}21$, $r_{0z} = -r_{0\bar{z}} = 2{\cdot}4$, $r_z = -r_{\bar{z}} = 4{\cdot}4$, and $(p_z^\circ|z|d_{z^2}) = 0{\cdot}2$, the moment $(\phi_z|ez|\phi_z^*)$ in the dichloro- case was calculated to be 1·58 and consequently the total of the squared moments was $2 \times 1{\cdot}58^2 = 5{\cdot}0$. The value 4·2 for the monochloro-case was obtained from a simplified calculation where all the parameter values are the same as before except $r_{\bar{z}} = -3{\cdot}8$ instead of $-4{\cdot}4$.

In case (ii), calculation in a similar manner gave the results in Table 5. Although, owing to the use of a less satisfactory set of functions, the approximation applied may not equally be justified as in the other cases, the results could be listed in such a table of rough estimation.

TABLE 5.—THE SQUARED TRANSITION MOMENT FOR THE FOURTH BAND

Complex	Observed	Calculated		
		Localized	Partly localized	Delocalized
$[Co(NH_3)_5Cl]^{2+}$	3·5	4·5	2·5	4·2
trans$[Co(NH_3)_4Cl_2]^+$	4·9	9·0	5·0	5·0
trans$[Co\ en_2Cl_2]^+$	5·3	(9·0)	(5·0)	(5·0)
$[Co(NH_3)_5Br]^{2+}$	3·7	5·6	2·6	4·3
trans$[Co\ en_2Br_2]^+$	4·0	(11·2)	(5·3)	(5·3)
$[Co(NH_3)_5\ I]^{2+}$	3·2	7·1	2·5	4·0

In view of the rather arbitrary choice of the parameter values for the numerical calculation, the results shown in Table 5 may include errors amounting to a factor of two or three, and consequently the agreement between the calculated and observed values may be considered satisfactory in every case. However, relative magnitudes of the calculated values would be only slightly affected by the arbitrariness in the choice of the parameter values. It is shown in Table 5 that, with the localized and partly localized models, the squared transition moment should be twice as large for the *trans*-dichloro-complex as for the monochloro- one; this may naturally be expected from the fact that the number of localized electrons to be transferred is twice as great for the former as for the latter. The observed values are not consistent with this result, and are more satisfactorily explained with the delocalized model. It seems reasonable to assume that the *trans*-dichloro-complex may be satisfactorily represented by the delocalized model and the monochloro-complex by an intermediate model between the partly localized (or the localized) and the delocalized one.

The squared transition moments for the bromo- and iodo-complexes were also calculated with the same assumption as was applied to the chloro-complexes, except that the cobalt–bromine distance was estimated to be 4·7 a.u. and the cobalt–iodine

Vol. 15 1960

distance 5·1 a.u. as compared with 4·4 a.u. for the cobalt–chlorine distance. It is very likely that the assumed degree of overlap of the orbitals is too high for the bromo- and iodo-complexes. This probable overestimation could very possibly be responsible for the calculated transition moments being too large.

Wave-numbers of the bands. It is almost impossible at present to prove the validity of the theory by calculating theoretical wave-numbers of the charge-transfer bands and comparing them with the observed wave-numbers; however, the assignment of the bands seems reasonable from Table 6, where the wave-numbers are compared with those of charge-transfer bands of halide ions in an aqueous solution. A more

TABLE 6.—WAVE-NUMBERS OF CHARGE-TRANSFER BANDS

X	Wave-number		Separation between the bands		
	X^- in aq. soln.	$[Co(NH_3)_5X]^{2+}$	X atom	X^- in aq. soln.	$[Co(NH_3)_5X]^{2+}$
Cl	55,200	36,500 44,050	880	—	7500(7500)*
Br	50,100 52,600	31,800 39,450	3700	2500	7700(6600)
I	44,300 51,500	26,110 34,930	7600	7200	8800(5100)

* The figures in parentheses are what the separation would be if there were no spin–orbit interaction.

or less quantitative support for the theory may be offered by consideration of the separation between the bands. It has been mentioned that in the bromo- and iodo-cases there is considerable spin–orbit interaction, which increases the energy separation of the two excited states related to the two bands. In parentheses in the last column of Table 6 are given the wave-number values that would be the separation of the bands in the absence of spin–orbit interaction. These values may approximately correspond to the energy difference between the halogen σ and π orbitals, or, if the π interaction is neglected, to half the bond energy (excluding the energy of ionic interaction). On this basis, the energy of the Co—Cl bond was estimated to be 15,000 cm^{-1} or about 40 kcal/mole, and if allowance is made for the π interaction† it may amount to 50–60 kcal/mole. This is in good agreement with the energy of the Cl—X bond where X is one of the rather electronegative elements, such as halogens, chalcogens and nitrogen. Moreover the smaller σ–π energy separation for a complex containing a heavier halogen is in agreement with the general tendency that the bond energy is smaller with element or compound molecules containing a heavier halogen.

On the other hand, the energy of co-ordination of tervalent cobalt and chloride can be estimated from thermo-chemical consideration. Since sufficient data are not available for direct calculation of the Co—Cl co-ordination energy, the Co—O co-ordination energy in the hexaquo complex of tervalent cobalt will first be calculated. The heat of formation of the hexaquo ion from the tervalent cobalt ion and water molecules, all in the gaseous state, was calculated in the way shown in Table 7. To obtain a co-ordination energy that may be compared with the bond energy, allowances

† The Co$d\pi$—Cl$p\pi$ interaction will not appreciably affect the bond energy, since both bonding and antibonding orbitals must be occupied. However, it will have the effect of decreasing the energy separation between the σ and π orbitals.

should be made for the promotion energy of the cobalt ion (from the ground quintet to the singlet corresponding to $(t_{2g})^6$, $^1A_{1g}$) and for the energy of the ligand-field stabilization, although they for the most part counterbalance each other to leave a net allowance of about 10,000 cm^{-1} per molecule. Thus the Co—O co-ordination energy is expected to be about 42,000 cm^{-1} or about 120 kcal/mole. To estimate the Co—Cl co-ordination energy the following reaction in an aqueous solution was considered:

$$[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5OH_2]^{3+} + Cl^-$$

From available data,[12] ΔH for this reaction was calculated to be $-2{\cdot}5$ kcal/mole, a magnitude that is almost negligible for the present problem. Since the total of the

TABLE 7.—CALCULATION OF THE HEAT OF FORMATION OF THE HEXAQUOCOBALT(III) ION IN THE GASEOUS STATE

$$\begin{array}{ccc} Co^{3+} + 6H_2O\ (\text{vapour}) + \text{aq} & \xrightarrow{\Delta H_f} & [Co(OH_2)_6]^{3+} + \text{aq} \\ \uparrow 6\Delta H_v & & \downarrow \Delta H_2 \\ Co^{3+} + \text{aq} & \xrightarrow{\Delta H_1} & [Co(OH_2)_6]^{3+}\,.\,\text{aq} \end{array}$$

$$\begin{aligned} \Delta H_f &= \Delta H_1 - 6\Delta H_v - \Delta H_2 \\ &= -394{\cdot}000 - 22{\cdot}000 + 155{\cdot}000 \\ &= -261{\cdot}000\ (cm^{-1}) \end{aligned}$$

ΔH_f: Heat of formation of $[Co(OH_2)_6]^{3+}$
ΔH_v: Heat of vaporization of H_2O
ΔH_1: Heat of hydration of Co^{3+} [11]
ΔH_2: Heat of hydration of $[Co(OH_2)_6]^{3+}$

negative heat of hydration is very much greater (about 320 kcal/mole greater) for the product of the reaction than for the reactant, the co-ordination energy should be correspondingly greater for the reactant than for the product; thus the energy of the Co—Cl co-ordination may amount to about 440 kcal/mole (about 320 kcal/mole greater than the Co—O co-ordination energy).

The reaction may be regarded as consisting of the following processes: (i) dehydration of $[Co(NH_3)_5Cl]^{2+}$ and vaporization of H_2O, (ii) breaking of the Co—Cl bond without affecting the Co—NH_3 bonds, (iii) formation of the Co—OH_2 bond without affecting the Co—NH_3 bonds, and (iv) hydration of the resulting species, $[Co(NH_3)OH_2]^{3+}$ and Cl^-. With this approximation, the difference in bond energy between the Co—Cl and Co—OH_2 would be the heat of the reaction minus the heat required in the (i) and (iv) processes.

In Table 8 are given the standard heats of formation (in aqueous solution) which are taken from the literature[12] and the heats of hydration which were estimated from the Born equation and the variation of dielectric constant of water with temperature. (The details of the method of calculation are given, for example, in ref. (9), p. 64.) Although, on account of the different conventions on which the two kinds of values are based, the heat of formation of any respective ionic species in the gaseous state cannot be given by simple subtraction of the values, such a difficulty should disappear for the whole reaction as a result of counterbalancing the biases due to the different standards of the two conventions.

[11] F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions* p. 67. John Wiley, New York (1958).
[12] F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE and I. JAFFE, *Selected Values of Chemical Thermodynamic Properties*. U.S. Department of Commerce, National Bureau of Standards (1952).

Vol. 15 1960

On the other hand, by an approach based on a simple ionic model of the complex, the electrostatic bond energy for the tervalent cobalt and chloride ions may be calculated to be about 430 kcal.

It is rather unexpected that the co-ordination energy estimated from thermochemical treatment and the electrostatic bond energy obtained by electrostatic calculation are in such good agreement. Although this may rather support an ionic model of the complex, it will not disprove the theory here developed in regard to the charge-transfer bands on the basis of the molecular orbital theory. The electrostatic

TABLE 8.—STANDARD HEATS OF FORMATION IN AQUEOUS SOLUTION AND HEATS OF HYDRATION

Species	Standard heat of formation ΔH_f° (kcal/mole)	Heat of hydration ΔH_{hyd} (kcal/mole)
$[Co(NH_3)_5Cl]^{2+}$	−162·1	−190
H_2O	− 68·3	− 10
$[Co(NH_3)_5OH_2]^{3+}$	−192·9	−430
Cl^-	− 40·4	− 90
difference between the former two and the latter two	−2·5	−320

effect of the central ion on a ligand electron is to a first approximation the same irrespective of the kind of orbital that the electron occupies, and the energy difference of the σ and π levels appears only in the second-order term of the interaction. Thus in the chloropentammine case, the energy difference between the chlorine σ and π orbitals was estimated to be about 16 kcal/mole (less than 4 per cent of the electrostatic bond energy) with a purely ionic model. This is much smaller than the observed. With an LCAO MO model, as mentioned above, the σ–π energy difference is of the same order of magnitude as half the bond energy (in the LCAO MO sense). From these considerations it may be concluded that regardless of the actual nature of the co-ordinate bond in the complex, which should be to some extent covalent and to some extent electrostatic, spectra of the complex can to a first approximation be interpreted with an LCAO MO model. This may be the case not only with the charge-transfer bands in question, but also with the first and second bands of cobalt (III) complexes previously discussed, and further with spectra of other metal complexes except complexes of highly ionic character.

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APPENDIX 1

In these calculations the Slater atomic orbitals with the parameter values as given below were assumed and mixing of the orbitals was neglected. The formulae derived for the transition moments are:

$$(p_x|ex|d_{z^2}) = \frac{(\rho_a\rho_b)^{7/2}R}{2^9\cdot 3\cdot\sqrt{15}}[(-3B_4+4B_2-B_0)A_7+(3B_5-8B_3+5B_1)A_6+$$
$$+(3B_6+4B_4-11B_2+4B_0)A_5+(-3B_7+4B_5+7B_3-8B_1)A_4+$$
$$+(-8B_6+7B_4+4B_2-3B_0)A_3+(4B_7-11B_5+4B_3+3B_1)A_2+$$
$$+(5B_6-8B_4+3B_2)A_1+(-B_7+4B_5-3B_3)A_0]$$

$$(p_x|ex|d_{x^2-y^2}) = \frac{(\rho_a\rho_b)^{7/2}R}{2^9\cdot 3\cdot\sqrt{5}}[(B_4-2B_2+B_0)A_7+(-B_5+2B_3-B_1)A_6+$$
$$+(-B_6+3B_2-2B_0)A_5+(B_7-3B_3+2B_1)A_4+$$
$$+(2B_6-3B_4+B_0)A_2+(-2B_7+3B_5-B_1)A_2+$$
$$+(-B_6+2B_4-B_2)A_1+(B_7-2B_5+B_3)A_0]$$

where $(p_x|ex|d_{z^2})$, for example, represents the transition moment in the x direction for the $p_x \rightarrow d_{z^2}$ jump of an electron without spin change, p_x being the chlorine $3p_x$ and d_{z^2} being the cobalt $3d_{z^2}$. Definitions of the other notations in these and the following expressions are the same as given by ROOTHAAN[12] in equations (15), (16) and (24) of his paper. The parameter values used are $\rho = \frac{1}{2}(\rho_a+\rho_b) = 9{\cdot}0$ and $9{\cdot}5$, $\tau\rho = \frac{1}{2}(\rho_a-\rho_b) = 0{\cdot}75$, and $R = \rho_a/\rho_a = \rho_b/\rho_b = 4{\cdot}4$ (a standing for d_{z^2} and b for p_x). The values given in Table 1 are within ± 20 per cent of the calculated values with either choice of the ρ values, and will not be appreciably different from the values calculated with other parameter values slightly different from those given above.

Concerning the $p\sigma \rightarrow d_{z^2}$ transition moment, a detailed discussion will be made with reference to Table 5, but here it is simply pointed out that the value of the moment may be a few tenths of eR, where e represents the unit charge and R the distance between the average positions of the orbitals, which is equal to 4·4 atomic units in this case.

The $p\sigma \rightarrow d_{z^2}$ electron jump with spin change that produces triplet states would be forbidden if there were no spin–orbit interaction. This is discussed in the text.

APPENDIX 2

The wave functions for the ground state and one of the charge-transferred states may be expressed as follows:

$$\Psi X = \psi_{core}\cdot p_0^{+}\cdot p_0^{-}\cdot p_1^{+}\cdot p_1^{-}\cdot p_{-1}^{+}\cdot p_{-1}^{-}$$
$$\psi(p_0^{+}\rightarrow d_0^{+}) = \psi_{core}\cdot d_0^{+}\cdot p_0^{-}\cdot p_1^{+}\cdot p_1^{-}\cdot p_{-1}^{+}\cdot p_{-1}^{-}$$

where the procedures for normalization and antisymmetrization were omitted to make the expression simple. ψ_{core} represents the wave function of the system consisting of all the ammonia electrons, the cobalt electrons that fully occupy the orbitals belonging to the K,L and M shells except the orbitals $3d_{x^2-y^2}$ and $3d_{z^2}$, the chlorine electrons that fully occupy the orbitals belonging to the K and L shells and the $3s$ orbital and all the nuclei. Here by the words cobalt, ammonia and chlorine are meant the atom, molecule and ion in the complex (not any of those in the free state). So the orbitals will mix with each other and with outer orbitals such as the chlorine $3p$, the coblat $3d_{z^2}$, $3d_{x^2-y^2}$, $4s$, $4p$, etc. to form molecular orbitals. p_0^{+}, for example, represents the wave function of the electron occupying the chlorine $3p$ orbital with zero angular momentum around the axis and having the spin quantum number $+\frac{1}{2}$, whereas d_0^{+} concerns the cobalt $3d$ orbital with similar meanings of the super- and subscript. Here again mixing of orbitals may occur. Although often in this paper the mixing of orbitals is not explicitly stated, the orbitals may be regarded as molecular orbitals. Except where otherwise stated, the effect of the mixing was considered to be not so great as to seriously affect the result.

[12] C. C. J. ROOTHAAN, *J. Chem. Phys.* **19**, 1445 (1951).

Vol. 15 1960

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DIPOLE MOMENTS AND STRUCTURES OF SOME *BIS*-(TRIFLUOROACETYLACETONATO) COMPLEXES

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Abstract—The dipole moments, in benzene solution, of *bis*-(trifluoroacetylacetonato)-Be(II), Co(II) and Cu(II) have been measured. The results are believed to indicate that, under the conditions of the measurements, the latter two exist as planar complexes with a *cis–trans* ratio of about 3 : 2. This is the same conclusion previously reached by MCCARTHY and MARTELL for the Cu(II) compound alone by an independent method.

THE *bis* complexes formed by trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione) may be of three structural types, namely, tetrahedral, *cis*-planar and *trans*-planar. In order to analyse our dipole moment data, it is convenient to consider, *formally*, a contribution to the total dipole moment by the C-CF_3 grouping μ_{CF_3}, and a contribution by the C-CH_3 grouping, μ_{CH_3}. If now we assume that in the tetrahedral case each chelate ring has the geometry of a regular hexagon while in the other cases the structural parameters are those found in $Fe(C_5H_7O_2)_3$ by ROOF[1], the following expressions for the net moments in terms of μ_{CF_3} and μ_{CH_3} may easily be derived:

Tetrahedral Case:

$$\mu = 2 \cos 30^\circ \cos 45^\circ |\mu_{CF_3} - \mu_{CH_3}|$$
$$= 1{\cdot}22\Delta$$

cis-Planar Case:

$$\mu = 2 \cos 33^\circ |\mu_{CF_3} - \mu_{CH_3}|$$
$$= 1{\cdot}68\Delta$$

trans-Planar Case:

$$\mu = 0$$

DISCUSSION

We have denoted $|\mu_{CF_3} - \mu_{CH_3}|$ by Δ. It is seen that only this difference and not the absolute values are involved. Even the quantity Δ, however, is artificial in the sense that it cannot be considered as truly constant independent of the environments of the CF_3 and CH_3 groups. This is because mutually polarizing interactions will always occur between a group such as CF_3 or CH_3 and the moiety to which it is connected. However, we believe it should be quite safe to assume that the effective value of $|\mu_{CF_3} - \mu_{CH_3}|$ is essentially independent of whether the chelate ring to which the CF_3 and CH_3 groups are attached is part of a planar or a tetrahedral *bis*-chelate system. Furthermore, it would also seem safe to assume that there will be no appreciable dependence of this quantity upon the specific metal ion involved since variations in the observed chemical shifts of ring protons in diverse acetylacetone complexes have been found to be almost negligible.[2]

[1] R. B. ROOF, JR., *Acta Cryst.* **9**, 781 (1956).
[2] R. H. HOLM and F. A. COTTON, *J. Amer. Chem. Soc.* **80**, 5658 (1958).

Consequently, we adopt the following method of analysing the results presented in Table 1. We assume that the value of Δ may be taken as 1/1·22 times the moment of the beryllium compound which is certainly tetrahedral. Since the moments of the Co(II) and Cu(II) compounds are far from zero, it is clear that they cannot have exclusively *trans*-planar configurations. We rule out the possibility of their having tetrahedral configurations. For the Cu(II) compound this is done on the basis of a vast amount of evidence[3,4] that, except under stress of unusual crystalline or steric forces, Cu(II) seems always to form planar rather than tetrahedral four-co-ordinate

TABLE 1.—DIPOLE MOMENT DATA FOR SOME *bis*-TRIFLUOROACETYLACETONATES IN BENZENE*

Compound	$_{\infty}P_2$ (cc)	P_E (cc)	P_O (cc)†	μ(D) ± 0·1†‡
Be	450·5	57·9	392·6	4·42 (0%)
			363·6	4·25 (50%)
Cu(II)	334·5	64·1	270·4	3·67 (0%)
			238·3	3·45 (50%)
Co(II)	296·5	60·8	235·7	3·42 (0%)
			205·3	3·19 (50%)

* Temperature: 29·8 ± 0·2°C; for benzene: specific polarization: 0·34086 cm^3,[12] specific refraction: 0·33544.
† P_A taken to be 0 and 50% P_E.
‡ Calculated from the relation $\mu = 0{\cdot}012812\sqrt{(P_O T)}$.

Vol. 15 1960

complexes, and further evidence from the observed electronic spectra[5,6] of β-diketone complexes of Cu(II). For the Co(II) compound this is done on the basis of the known magnetic and spectral properties of the compound[7] and a comparison of these both with theory[8,9] and with experimental data[7,8,9] for a large number of Co(II) complexes of known configurations. The only remaing alternative then seems to be to assume that the observed moments indicate that, in benzene solution at ~25°, both the Co(II) and Cu(II) complexes exist as a mixture of *cis*- and *trans*-planar forms. Finally, we can make an estimate of the fraction of the *cis*-form by using the relations given above. Since the *cis*-form should have a moment of $\sim 1{\cdot}68\,\Delta$ which is ~5·9 D, the results suggest that the fraction of the *cis*-form is about 3·5/5·9 ≈ 60 per cent for the Cu(II) complex and 3·2/5·9 ≈ 54 per cent for the Co(II) complex.

It is interesting to note that MCCARTHY and MARTELL[10] arrived at the same approximate 60 per cent *cis–trans* ratio for the Cu(II) compound in an independent fashion. They measured the dipole moments in benzene solution of two Schiff base complexes of Cu(II) with the following results: The difference of 5·07 D, equivalent to our $1{\cdot}68\,\Delta$ value can then be attributed to the two uncompensated *cis* CF_3—C and CH_3—C bonds. Cu(II) trifluoroacetylacetonate was found to have a moment of 3·06 D,

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[4] L. E. ORGEL and J. D. DUNITZ, *Nature, Lond.* **179**, 462 (1957).
[5] R. L. BELFORD, A. E. MARTELL and M. CALVIN, *J. Inorg. Nucl. Chem.* **2**, 11 (1956).
[6] R. L. BELFORD, M. CALVIN and G. BELFORD, *J. Chem. Phys.* **26**, 1165 (1957).
[7] R. H. HOLM and F. A. COTTON. *J. Amer. Chem. Soc.* In press.
[8] C. J. BALLHAUSEN and C. K. JØRGENSEN, *Acta Chem. Scand.* **9**, 397 (1955).
[9] R. H. HOLM and F. A. COTTON, *J. Chem. Phys.* **31**, 788 (1959); **32**, 1168 (1960).
[10] P. J. MCCARTHY and A. E. MARTELL, *J. Amer. Chem. Soc.* **78**, 2106 (1956).

so that the ratio 3·06/5·07 produced a 60 per cent *cis* distribution. Therefore, although the values of the dipole moment of the Cu(II) compound are somewhat different, each predicts the same approximate *cis-trans* ratio relative to its own set of measurements.

$R_1 = R_2 = R_3 = R_4 = CH_3$; $\mu = 4{\cdot}53$ D
$R_1 = R_2 = CF_3$
$R_3 = R_4 = CH_3$; $\mu = 9{\cdot}60$ D

Finally, the question of why an existing and almost certainly more accurate value of $|\mu_{CF_3} - \mu_{CH_3}|$ was not used in the preceding analysis may now be raised. Methylfluoroform, CF_3CH_3 has been shown to have a dipole moment of 2·32 D by microwave spectroscopy.[11] If this value were taken for Δ, tetrahedral and *cis*-planar *bis*-trifluoroacetylacetonates should have moments of 2·86 and 3·89 D, respectively, and for the Cu(II) compound the distribution of the *cis* form becomes ~90 per cent. It is believed that D = 2·32 is inappropriate here since two independent sets of measurements in solution strongly indicate that it must be 1·5–2 times as large in these acetylacetonato complexes. This inappropriateness is doubtless connected with the fact, mentioned previously, that Δ is not a true constant but is susceptible to polarizability effects which it may be assumed occur when a strongly electrophilic group like $-CF_3$ is directly appended to the σ-skeleton of a mobile π-system such as is believed to exist in acetylacetonato complexes.[2]

EXPERIMENTAL

The dielectric constant of pure benzene and the benzene solutions were measured by the heterodyne beat method.[12] The cell used was equipped with platinum electrodes and had a capacitance of 110 $\mu\mu$F. Analytical reagent benzene was further purified by allowing it to stand over freshly cut sodium for a few days and then partially freezing it. The solid residue obtained by decantation was remelted in contact with clean sodium and then used. Solutions were made up on a Mettler balance accurate to 0·02 mg. Densities were measured pycnometrically to $\pm 0{\cdot}0003$ g/ml. Indices of refraction were measured on an Abbé refractometer using the sodium *D*-line as a source. No significant optical exaltation of refraction was observed in the coloured solutions of the copper and cobalt compounds since determination of the total molar polarization by summation of the bond refractivities of Vogel *et al.*[13] and the refractivities of metal atoms given by McCarthy and Martel[10] give results only 1–2 cm³ different from those calculated from R_D. All measurements were thermostated to $29{\cdot}8 \pm 0{\cdot}2$°C.

The dipole moments of the three compounds were calculated according to LeFevre[12] from measurements of the total polarization and electronic polarization. In the final calculation it is necessary of course to assume the atom polarization to be some fraction of the electronic polarization. Finn, Hampson and Sutton[14] have shown that in benzene metal acetylacetonates possess anomalously high atom polarizations. From this work we assume $P_A = 50\% P_E$ for the trifluoro compounds.

Preparation of compounds

Bis-(trifluoroacetylacetonato) Be(II). This compound was prepared according to the procedure of Arch and Young[15] for the unfluorinated compound. Trifluoroacetylacetone was obtained from

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[12] R. J. W. LeFevre, *Dipole Moments*. Methuen, London (1953).
[13] A. I. Vogel, W. T. Kresswell, G. J. Jeffery and J. Leicester, *Chem & Ind.* 358 (1950).
[14] A. E. Finn, G. C. Hampson and L. E. Sutton, *J. Chem. Soc.* 1254 (1938).
[15] A. Arch and R. C. Young, *Inorganic Synthesis* Vol. 2, p. 17. McGraw-Hill, New York (1946).

the Columbia Chemical Company. The crude product was recrystallized from benzene–light petrol and then sublimed twice at 100° and <1 mm to yield a perfectly white crystalline product m.p. 113°. Found: C, 38·47; H, 2·96. Calc. for $Be(C_5H_4O_2F_3)_2$: C, 38·11; H, 2·54%).

Bis-(trifluoroacetylacetonato) Cu(II). Prepared by the method of BELFORD *et al.*[15] which yielded a blue powdery material. (Found: Cu, 16·9. Calc. for $Cu(C_5H_4O_2F_3)_2$: Cu, 17·14%).

Bis-(trifluoroacetylacetonato) Co(II). The compound was obtained as a hydrate by reacting an aqueous solution of cobalt(II) acetate with an ethanolic solution of trifluoroacetylacetone. An orange crystalline product immediately precipitated. This was recrystallized twice from ethanol–water. (Found Co, 14·0; C, 29·48; H, 3·46. Calc. for $Co(C_5H_4O_2F_3)_2 \cdot \frac{5}{2}H_2O$: Co, 14·37; C, 29·28; H, 3·19%). The hydrate was dehydrated by heating *in vacuo* at 58° C for 12 hr to produce the deep red-brown anhydrous complex. (Found: Co, 16·4; C, 32·90; H, 2·38. Calc. for $Co(C_5H_4O_2F_3)_2$: Co, 16·14; C, 32·90; H, 2·21%).

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Vol. 15 1960

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SOLVATES OF URANIUM TETRACHLORIDE WITH PHOSPHORUS OXYCHLORIDE*

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Abstract—Two compounds of uranium tetrachloride and phosphorus oxychloride, the solvates, $UCl_4 \cdot 4POCl_3$ and $UCl_4 \cdot POCl_3$ are reported. The tetra-solvate is an aqua-green tetragonal crystalline material with indices of refraction of $n_o = 1{\cdot}645$, $n_e = 1{\cdot}657$. The material melts at 340°C (closed tube), following partial liquefaction and resolidification at 118°C.

The mono-solvate $UCl_4 \cdot POCl_3$ was prepared from the tetra-solvate by gentle heating under high vacuum. This material is light blue-green. Its symmetry class is unknown. Indices of refraction are: maximum index 1·660, minimum index: 1·645. It occurs in irregularly shaped crystals. Powder X-ray data are reported for these two compounds. The possible existence of other solvates in the series is discussed.

WHILE conducting electrolytic experiments in phosphorus oxychloride, $POCl_3$, CADY and TAFT discovered that solution of various halides in this solvent resulted in a variety of crystalline and gelatinous compounds.[1] Phosphorus oxychloride has recently been utilized in various metathetical reactions, solvate preparation and in studies of acid–base properties in non-aqueous solvents.[2–5] The compounds $3ZrCl_4 \cdot 2POCl_3$ and $3HfCl_4 \cdot 2POCl_3$ have been used to effect an efficient separation of zirconium and hafnium via fractional distillation.[6] Typical solvates of phosphorus oxychloride known to form are $GaCl_3 \cdot POCl_3$, $AlCl_3 \cdot POCl_3$, $TiCl_4 \cdot 2POCl_3$, $TeCl_4 \cdot POCl_3$ and $AlSbCl_8 \cdot 3POCl_3$.[7]

EXPERIMENTAL

Because of the hygroscopic nature of the complex uranium chlorides, prepared samples were transferred from weighing bottles into 100 ml volumetric flasks in a dry-box. The samples were then dissolved in 5 N nitric acid cooled to −10°C. This procedure prevented loss of hydrogen chloride. After solution was complete the uranium was oxidized to the uranyl state by gentle heating or through the addition of a few drops of 3 per cent hydrogen peroxide. The solution was then diluted to the mark and aliquot portions of the solution taken as required for the analyses.

Methods of analysis

Uranium. Uranium was weighed as the ignited uranyl pyrophosphate following its precipitation as uranyl phosphate[8] in a solution buffered at pH 5 with ammonium acetate.

* Taken in part from a dissertation submitted by R. E. PANZER to the Graduate School of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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[1] H. P. CADY and R. TAFT, *J. Phys. Chem.* **29**, 1065 (1925).
[2] V. GUTMANN, *Ostereichische Chem. Z.* **56**, 126 (1955).
[3] V. GUTMANN, *J. Phys. Chem.* **63**, 378 (1959).
[4] J. C. SHELDON and S. Y. TYREE, JR., *J. Amer. Chem. Soc.* **81**, 2290 (1959).
[5] N. N. GREENWOOD and K. WADE, *J. Inorg. Nucl. Chem.* **3**, 249 (1957).
[6] D. M. GRUEN and J. S. KATZ, *J. Amer. Chem. Soc.* **71**, 3843 (1949).
[7] J. R. VANWAZER, *Phosphorus and its Compounds* Vol. 1, *Chemistry*. Interscience, New York (1958).
[8] C. J. RODDEN (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, NNES, Plutonium Project Record, Div. VIII, Vol. 1. McGraw-Hill, New York (1950).

Phosphorus. Determined by precipitation as ammonium phosphomolybdate which was filtered, washed and ignited at 425°C to the weighing form, phospho-molybdic anhydride, $P_2O_5 \cdot 24MoO_3$.[9]

Chloride. Determined by the usual gravimetric method of precipitation from nitric acid solution with silver nitrate.[10]

X-ray methods

Powder X-ray photographs were obtained using Cu-K_α radiation. The camera had a radius of 57·3 mm, film was Eastman Kodak No-screen type mounted by the Straumanis method. Exposure times were as noted with the data from each sample. The X-ray data have been deposited with the A.S.T.M. X-ray Powder Data File, Pennsylvania State University, University Park, Pa., U.S.A.

Optical investigations

Optical crystallographic investigations were made using a polarizing microscope. Indices of refraction of the crystals were determined on the microscope stage by the immersion method. It was found that by working rapidly the indices could be determined before the compounds reacted with the index media. In addition, it was discovered that the compounds do not rapidly react with the high-index-range media. For general study a mineral oil suspension of the crystals on a glass slide was covered with a thin cover glass; it was thus possible to maintain the crystals unchanged for an hour or more.

Purification of phosphorus oxychloride

This solvent was purified by distilling through a seven stage bubble column at least three times before use. The first fraction containing most of the hydrogen chloride was discarded. Finally, the solvent was distilled directly into the vessel, (previously flame dried under vacuum), in which it was to be used.

Preparation of uranium tetrachloride

This compound was prepared by the method of HERMANN and SUTTLE[11].

RESULTS

The solvate, $UCl_4 \cdot 4POCl_3$

During investigations of the compound, $UCl_5 \cdot PCl_5$, solutions of UCl_4 in $POCl_3$ were prepared for use in studies of the absorption spectra of UCl_4, UCl_5 and UCl_6 dissolved in phosphorus oxychloride.[12] Uranium tetrachloride dissolved in $POCl_3$ with subsequent appearance of a pale green precipitate. This material was found to be a solvate of uranium tetrachloride with phosphorus oxychloride. The formula is $UCl_4 \cdot 4POCl_3$. (Found: U, 23·6; Cl, 57·3; P, 12·2. Calc. U, 24·0; Cl, 56·8; P, 12·4%). The molecular weight was not determined because no cryoscopic medium was found in which the compound was sufficiently soluble without ionization or reaction with the solvent.

When heated in a sealed tube the material appeared to partially liquefy at 118°C with a drop of liquid appearing at the top of the tube. The sample lightened in colour with further heating and melted at 340°C to a light green liquid.

An optical crystallographic investigation gave the following data.

The compound is light green in plane polarized light; interference colours are first order greys to first order yellows; birefringence is low, the elongated crystals being length fast; extinction is parallel to the zone of elongation.

[9] I. M. KOLTHOFF and E. B. SANDELL, *Textbook of Quantitative Inorganic Analysis* (3rd Ed.). Macmillan, New York (1952).
[10] N. H. FURMAN (Editor), *Scott's Standard Methods of Chemical Analysis* Vol. 1. Van Nostrand, Princeton (1948).
[11] J. A. HERMANN and J. F. SUTTLE, *Inorganic Synthesis* (Editor-in-chief T. MOELLER), Vol. 5, p. 143. McGraw-Hill, New York (1957).
[12] R. E. PANZER, Doctoral dissertation, University of New Mexico (1958).

Indices of refraction: $n_e = 1{\cdot}645$ (fast direction); $n_o = 1{\cdot}657$ (slow direction); birefringence = 0·012.

The crystals are uniaxial and the optical sign is negative. The existence of interference figures, together with the values of $\sin^2\theta$ which occur in multiples of 0·0080 for the first five lines in the X-ray powder pattern, indicate that the solvate compound is tetragonal. However, the occurrence of an isometric material sometimes mixed with the tetragonal crystals has created an ambiguity in the complete interpretation of the X-ray data. It is expected that further investigations of this solvate system will clarify the situation.

The solvate, $UCl_4 \cdot POCl_3$

When the tetra-solvated compound described above was heated to 50°C under a pressure of 0·5 μ another solvate formed which had the composition, $UCl_4 \cdot POCl_3$. It was light blue in colour. Analysis of this compound was as follows. (Found: U, 44·8; Cl, 45·6; P, 6·17. Calc. U, 44·6; Cl, 46·5; P, 5·82%).

When this solvate was heated in a sealed tube the following phenomena were observed. At 280°C the sample darkened in colour and appeared to shrink; it melted at 340°C to a green liquid which became light green on cooling. This solid, investigated under a polarizing microscope was found to be isotropic and light yellow green in plane polarized light. It is thus isometric crystalline or amorphous.

Optical data were obtained on the solvate, $UCl_4 \cdot POCl_3$. It is pale bluish green in plane polarized light; interference colours are first-order greys to first order yellows; extinction is wavy and not complete for the entire crystal. No optical sign was determinable because no optical figure could be observed. Most of the crystals were irregularly shaped, though some were tabular.

Indices of refraction: maximum index = 1·660; minimum index = 1·645; birefringence = 0·025.

The symmetry class of the crystals is unknown. The method of preparation of the mono-solvated uranium tetrachloride, i.e., heating the tetra-solvated uranium tetrachloride to remove three molecules of phosphorus oxychloride is not conducive to the formation of well-defined crystals.

In some batches of these solvates a different material was observed under the microscope, intermixed with the solvates reported here. This material is isotropic in plane polarized light and appeared to be isometric crystalline. It appears that there are other solvates in this system in addition to the two which have been characterized.

DISCUSSION

GUTMANN[13] has stated that so far no known compound solvated with phosphorus oxychloride has more than three molecules of the solvent attached to it. In explanation he advances the theory that the high molar volume of phosphorus oxychloride, 97·5 cm^3, prevents close co-ordination of more than three molecules of that solvent. The compound, $UCl_4 \cdot 4POCl_3$ is the first phosphorus oxychloride solvate reported in which four molecules of the solvent are attached to one of the solute. The large co-ordination sphere of uranium apparently allows close approach of the four solvate molecules to the extent that they are readily co-ordinated.

[13] V. GUTMANN, *Ostereichische Chem. Z.* **56**, 128 (1955).

LINDQUIST and BRANDEN have determined that the co-ordination of solvent molecules may also take place through the oxygen atom, i.e., $Cl_3POSbCl_5$.[14]

Further investigations of the system UCl_4–$POCl_3$ should be conducted to elaborate all the solvates existing in this system. The structures of these may also be found to involve co-ordination through the oxygen atom.

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[14] I. LINDQUIST and C. E. BRANDEN, *Acta Chem. Scand.* **12**, 134 (1958).

Vol.
15
1960

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THE THERMAL STABILITY OF METAL AMMINES—I

PENTAMMINECHLOROCHROMIUM(III) CHLORIDE

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Abstract—Thermogravimetric analysis indicates the loss of two moles of NH_3 from $[Cr(NH_3)_5Cl]Cl_2$ at about 250°C in air followed by complete loss of NH_3 as the temperature is raised. At constant temperatures of 150, 200 and 300°C in air, however, decomposition is essentially smooth with no arrests indicated for intermediate ammines. Nevertheless it is possible to isolate a material with empirical composition $Cr(NH_3)_5Cl_3$ by careful thermal treatment of $[Cr(NH_3)_5Cl]Cl_2$ in air followed by washing with water and HCl. This product differs from that formed by thermal treatment of $[Cr(NH_3)_5Cl]Cl_2$ in anhydrous HCl. The latter is not a monomeric isomer of $Cr(NH_3)_5Cl_3$ as previously suggested.[1] At 200°C the decomposition is zero order for the removal of the last three NH_3 molecules from $[Cr(NH_3)_5Cl]Cl_2$. There is no kinetic differentiation among these three NH_3 molecules within the accuracy of the data. Decomposition temperatures obtained by thermogravimetric analysis should be interpreted with care because of the relatively rapid heating rates customarily employed.

SCHLESINGER and WORNER[1] investigated the thermal decomposition of $[Cr(NH_3)_5Cl]Cl_2$ in an atmosphere of anhydrous HCl, but no comparable study of the thermal decomposition of this material in air has been reported. In order to get some idea of the resistance of chromium(III)–ammonia bonds to thermal degradation the thermal decomposition in air of $[Cr(NH_3)_5Cl]Cl_2$ and of the light green "$[Cr(NH_3)_3Cl_3]$" prepared from it by a modification of SCHLESINGER and WORNER's method was studied by thermogravimetric analysis and at fixed temperatures.

EXPERIMENTAL

$[Cr(NH_3)_5Cl]Cl_2$ was prepared according to PALMER[2]. (Found: Cr, 20·3; Cl, 43·5; NH_3, 33·9. Calc. for $[Cr(NH_3)_5Cl]Cl_2$: Cr, 21·3; Cl, 43·7; NH_3, 35·0%.

$Cr(NH_3)_5Cl_3$ was prepared by a modification of the method of WORNER[3] in which $[Cr(NH_3)_5Cl]Cl_2$ was heated rapidly with stirring in contact with 150 per cent of the stoicheiometric requirement of anhydrous HCl for 1–2 min after maximum negative pressure was achieved. The reaction mixture was then washed successively with H_2O at 35°C, 5% aq. HCl, and acetone to remove any NH_4Cl and $3NH_4Cl{\cdot}2CrCl_3$ formed and unreacted $[Cr(NH_3)_5Cl]Cl_2$. Recovery averaged 60 per cent. (Found: Cr, 24·5; Cl, 50·5; NH_3, 25·5. Calc. for $Cr(NH_3)_5Cl_3$: Cr, 24·8; Cl, 50·8; NH_3, 24·4%.) The material used in the higher fixed temperature studies analysed Cr, 23·0 and Cl, 49·2%.

Two grammes of the "$[Cr(NH_3)_5Cl_3]$" analysing Cr, 24·5, Cl, 50·5 and NH_3, 25·5% was dissolved in 80 ml H_2O at 50–60°C with stirring. The clear solution was cooled in tap water and concentrated by evaporation under an air stream at room temperature for about 20 hr. The nearly dry residue was slurried in a small portion of H_2O and the crystals separated by sucking them "dry" on a fine sintered-glass crucible, after which they were washed with acetone and air dried. Brick red crystals were

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[2] W. G. PALMER, *Experimental Inorganic Chemistry* p. 198. Cambridge University Press (1954).
[3] R. K. WORNER, Thesis, University of Chicago (1925).

recovered; 0·72 g yield. (Found: Cr, 18·3; Cl, 42·6; NH_3, 24·4; H_2O, 14·7 (by diff.) ; Calc. for $[Cr(NH_3)_5(H_2O)_2]Cl_3$: Cr, 19·7; Cl, 40·4; NH_3, 19·4; H_2O, 20·5%. Calc. for $[Cr(NH_3)_4(H_2O)_2]Cl_3$: Cr, 19·9; Cl, 40·5; NH_3, 25·9; H_2O, 13·7%.)

The thermogravimetric analysis (TGA) was conducted in a Chevenard thermobalance at a heating rate of about 150°C/hr. $[Cr(NH_3)_5Cl]Cl_2$ showed a partial arrest in weight loss corresponding to the loss of $2NH_3$ groups, and a less pronounced plateau corresponding to the formation of CrOCl (or $Cr_2O_3{\cdot}CrCl_3$). "$[Cr(NH_3)_3Cl_3]$" showed a slight arrest in weight loss corresponding to CrOCl formation. The final decomposition product in both cases was Cr_2O_3 as identified by X-ray diffraction. No detectable weight loss occurred below 250°C in either case. Apparent loss of $2NH_3$ molecules from $[Cr(NH_3)_5Cl]Cl_2$ took place at about 300°C and possible formation of CrOCl occurred at

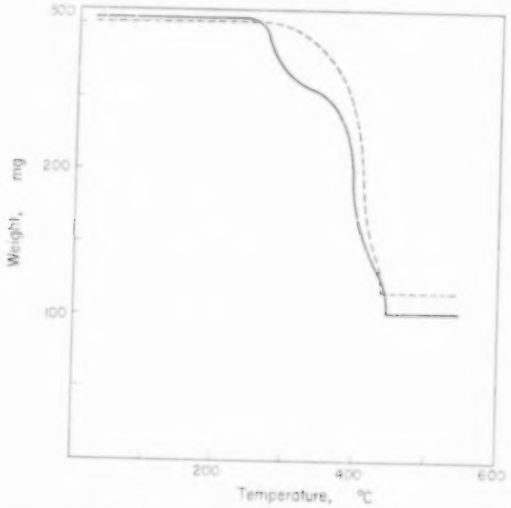

FIG. 1.—Thermogravimetric analysts of $[Cr(NH_3)_5Cl]Cl_2$ (solid line) and "$[Cr(NH_3)_3Cl_3]$" (broken line) in air. Heating rate 150°C/hr.

425–440°C with $[Cr(NH_3)_5Cl]Cl_2$ and at 420–430°C with "$[Cr(NH_3)_3Cl_3]$". In both cases, final decomposition to Cr_2O_3 followed immediately after these partial arrests in weight loss, at 440° and 430°, respectively. Final weight losses were low by about 3 per cent compared to calculated losses for the formation of Cr_2O_3. These results are shown in Fig. 1.

Decomposition of both materials at the fixed temperatures of 150°, 200° and 300°C was conducted in a Weber laboratory oven in the first case and, for the higher temperatures, in a muffle furnace controlled by an Amplitrol regulator. At 150°C ±1° (Fig. 2), no well-defined arrest in weight loss was observed, and losses were somewhat irregular. Possible discontinuities occur at weights corresponding to the loss of $5NH_3$ from $[Cr(NH_3)_5Cl]Cl_2$ and to the formation of CrOCl. The residues gave poor X-ray patterns. At 195°C ± 10°, there is again an indication of partial arrest in weight loss corresponding to CrOCl formation for both materials. (Fig. 3). The residues, which represented incomplete conversion to Cr_2O_3, analysed for $[Cr(NH_3)_5Cl]Cl_2$: Cr, 56·4; Cl, 2·2 and for "$[CrNH_3Cl_3]$": Cr, 53·8, Cl, 1·9%. At 285°C ± 15°, $[Cr(NH_3)_5Cl]Cl_2$ decomposed rapidly until the composition Cr_2O_3 was approached. Thermal decomposition of "$[Cr(NH_3)_3Cl_3]$", however, appeared to take place non-uniformly, resulting in localized dark areas resembling Cr_2O_3 amid relatively unchanged material. This compound, therefore, was not fully studied at this temperature (Fig. 4) and final residues were not analysed. These data show that the rate of thermal decomposition in air of both $[Cr(NH_3)_5Cl]Cl_2$ and "$[Cr(NH_3)_3Cl_3]$" increases sharply at temperatures somewhat over 150°C.

Only the data from the 200°C run gave usable kinetic results. At 150°C there was too great a scatter in values, presumably because the temperature was not sufficiently constant over the long periods of time involved. At 300°C the reaction rate was too rapid for the technique used to give sufficient data. The results of the kinetic analysis are given in Table 1.

Vol. 15 1960

During the 200°C study it was observed that 30 min heating resulted in a 14 ± 2 per cent weight loss from $[Cr(NH_3)_5Cl]Cl_2$ corresponding to the loss of two molecules of NH_3 and the formation of a light green product closely resembling SCHLESINGER and WORNER's product. Purification of this material by washing with H_2O at 35°C, 5% aq. HCl and acetone gave an 82·6 per cent recovery of a

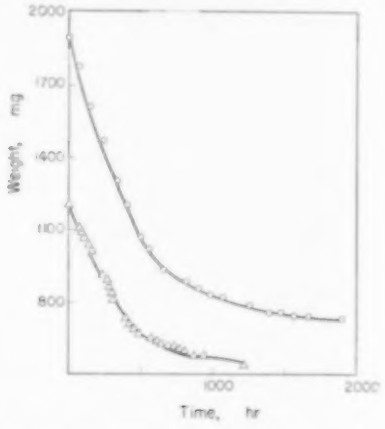

FIG. 2.—Decomposition of $[Cr(NH_3)_5Cl]Cl_2$ (circles) and "$[Cr(NH_3)_5Cl_3]$" (triangles) at 150°C in air.

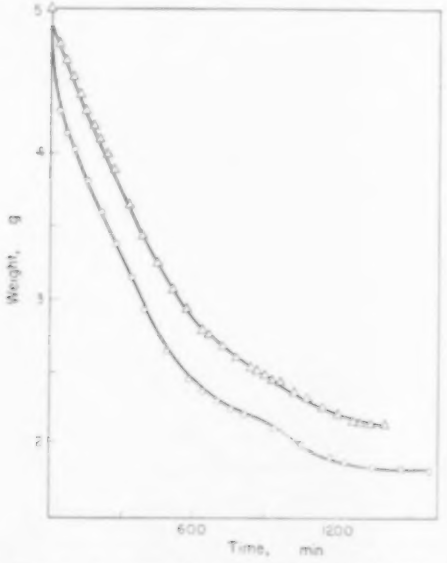

FIG. 3.—Decomposition of $[Cr(NH_3)_5Cl]Cl_2$ (circles) and "$[Cr(NH_3)_5Cl_3]$" (triangles) at 200°C in air.

powder containing 24·2% Cr and 46·0% Cl by elemental analysis. This material appeared homogeneous under a microscope and gave an X-ray pattern different from those of $[Cr(NH_3)_5Cl]Cl_2$ and "$[Cr(NH_3)_5Cl_3]$".

DISCUSSION AND CONCLUSIONS

Over a temperature range corresponding to decomposition of $[Cr(NH_3)_5Cl]Cl_2$ to Cr_2O_3 in 1½ to over 2000 hr, weight loss versus time curves are essentially smooth.

Decomposition of "$[Cr(NH_3)_3Cl_3]$" under the same conditions parallels this behaviour. Exposure of these materials during heating to an atmosphere of their gaseous decomposition products may have influenced the results. Gaseous decomposition products consisted of, first, white strongly alkaline fumes and, later, a strongly acidic gas, probably NH_3 and then NH_4Cl or HCl.

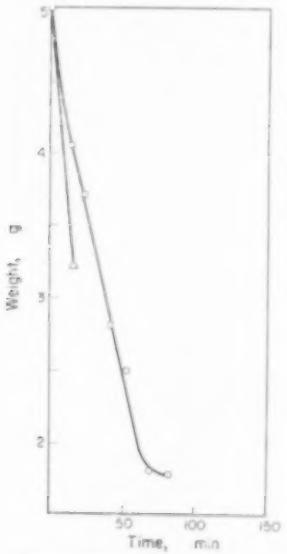

FIG. 4.—Decomposition of $[Cr(NH_3)_5Cl]Cl_2$ (circles) and "$[Cr(NH_3)_3Cl_3]$" (triangles) at 300°C in air.

TABLE 1.—RATE OF AMMONIA LOSS FROM CHROMIUM(III) AMMINES AT 200°C

	$[Cr(NH_3)_5Cl]Cl_2$						$Cr(NH_3)_3Cl_3$							
Time (min)	30	60	92	150	210	270	30	60	90	120	150	180	210	240
$\frac{\Delta \text{ Mole } NH_3 \text{ lost}}{\Delta t} \times \left(\frac{\text{mole}}{\text{min}} \times 10^5\right)$	139	29	20	21	22	21	49	23	22	22	24	22	15	24
$\frac{\text{Total mole } NH_3 \text{ lost}}{\text{Mole Cr}}$	2·03	2·46	2·78	3·38	4·01	4·64	0·62	0·91	1·18	1·45	1·74	2·02	2·21	2·51

The data from Table 1 are not sufficient to permit extensive conclusions to be drawn about the course of the decomposition at 200°C. There is a difference in the rate of loss of the first two ammonia molecules compared to the remaining NH_3 molecules in $[Cr(NH_3)_5Cl]Cl_2$, but the data are not adequate for elucidation of this part of the process. The loss of NH_3 is zero order for both materials, with a rate of about 2×10^{-4} mole/min for each, if the first measurement in each system is neglected. This order is reasonable for a thermal decomposition and indicates that intramolecular bond breaking controls the reaction. Because the rate is essentially constant for the loss of most of the NH_3 from the $Cr(NH_3)_3Cl_3$ composition, there is energetically little difference in removing any one of the three NH_3 molecules. This implies that any

Vol. 15 1960

intermediate lower ammines of $CrCl_3$ decompose more rapidly than does $Cr(NH_3)_3Cl_3$ at 200°C.

It is interesting to note that TGA indicated both ammines to be stable below 250°C, whereas the constant temperature experiments showed marked instability at 200°C. This is undoubtedly due to the relatively rapid rate of heating employed in TGA and emphasizes the caution required in interpreting TGA results in terms of practical thermal stability. In this case, for example, the chromium ammines exhibited no loss of weight up to 250°C in TGA, but they lost 35 per cent in weight in 5·1 and 7·4 hr at 200°C. The TGA decomposition temperature, then, is one at which extensive decomposition occurs in 1 or 2 hr.

The structure of the $Cr(NH_3)_3Cl_3$ produced by heating $[Cr(NH_3)_5Cl]Cl_2$ in HCl is probably not an isomer of WERNER's $[Cr(NH_3)_3Cl_3]$[4] as postulated by SCHLESINGER and WORNER[1]. While our analyses agree empirically with such a formulation, analysis of the aquated product corresponds to $[Cr(NH_3)_3(H_2O)_2]Cl_3$ rather than to the expected $[Cr(NH_3)_3(H_2O)_3]Cl_3$. This suggests that the "$Cr(NH_3)_3Cl_3$" is really an ionic species such as $[Cr(NH_3)_4Cl_2][Cr(NH_3)_2Cl_4]$ rather than the neutral complex. If the inertness of chromium(III) complexes toward substitution[5] is considered in conjunction with the inability to replace co-ordinated H_2O with NH_3 on chromium(III) in aqueous solution, it is apparent that a tetraamine of chromium(III) could not result from a triammine under the conditions of aquation used. The "triammine" formed, then, must contain a cation which has four or five NH_3 ligands per chromium.

Another product with the same composition results upon careful heating of $[Cr(NH_3)_5Cl]Cl_2$ in air rather than in HCl. Since it is the same colour as SCHLESINGER and WORNER's product and differs only in X-ray diffraction pattern, there is always the possibility that the difference in the two is in the crystal lattice rather than in the structure of ions.

Acknowledgements—This work was supported in part by the Office of Naval Research. The authors are indebted to G. MINCARELLI for assistance with the experimental work, Dr. J. R. SOULEN for the TGA results, and the Analytical Department of Pennsalt Chemicals Corporation for the analyses.

[4] A. WERNER, *Ber. Dtsch. Ges. Chem.* **43**, 2286 (1910).
[5] H. TAUBE, *Chem. Rev.* **50**, 99 (1952).

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 76 to 81. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL STABILITY OF METAL AMMINES—II

COBALT(II) AND COBALT(III) COMPOUNDS

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Abstract—The thermogravimetric behaviour of $Co(py)_2Cl_2$, $Co(bipy)Cl_2$, Co(2,2′-iminodiypridine)Cl_2, $[Co(NH_3)_6]Cl_3$, *cis*-$[Co(NH_3)_4Cl_2]Cl$, *trans*-$[Co(NH_3)_4Cl_2]Cl$ and $Co(NH_3)_4PO_4$ has been examined in a nitrogen atmosphere. Chelation increases thermal stability, and, in addition, the six-membered 2,2′-iminodipyridine complex of $CoCl_2$ shows greater stability than the analogous 2,2′-bipyridine complex. In all cases examined the ammines of cobalt(III) began to lose weight well under 200°C. No significant difference was detected in the thermal behaviour of the *cis* and *trans* forms of $[Co(NH_3)_4Cl_2]Cl$. The salient features of the thermogravimetric curves are discussed.

Two extensive thermal studies of cobalt(III) ammines have recently appeared in the literature. WENDLANDT[1] has reported the results of heating fifteen compounds in air in a thermobalance of his own design. LOBANOV and his co-workers[2] have published the results of a differential thermal analysis of twenty-four cobalt ammines. Four of these compounds were included in the series covered by WENDLANDT. LOBANOV's paper does not specify the atmosphere used in the differential thermal analysis.

The present study included one compound, $[Co(NH_3)_6]Cl_3$, covered by both WENDLANDT and LOBANOV and six examined by neither of the above authors. Three of the materials examined in this work were cobalt(II) compounds. The present work was done in an atmosphere of nitrogen.

Vol. 15 1960

EXPERIMENTAL

Apparatus

The thermogravimetric curves were determined on a Chevenard Thermobalance. A nickel muffle was placed in the furnace, and a slow stream of dry high-purity nitrogen was passed through this to exclude oxygen. The muffle completely surrounded the sample except for a small opening in the bottom which allowed free passage of the crucible support and also served as an outlet for the gas stream. The exit gases were checked periodically with wet "Alkacid" paper. The furnace temperature controller was set at a heating rate of 300°C/hr.

Materials

Bis(pyridine)dichlorocobalt(II). $Co(py)_2Cl_2$ was prepared by slowly adding 90 g of anhydrous pyridine to 70 g of anhydrous $CoCl_2$ dissolved in 500 ml of absolute ethanol. The violet precipitate which formed was recovered by filtration and dried over P_2O_5. The weight of the recovered material was 112 g (72 per cent yield). No attempt was made to recover the remaining product dissolved in the ethanol. The crude product was recrystallized from warm anhydrous acetone and vacuum dried at room temperature before use. (Found: Co, 20·6; Cl, 24·1. Calc. for $Co(py)_2Cl_2$, Co, 20·5; Cl, 24·6%.)

2,2′-*Bipyridinedichlorocobalt*(II). $Co(bipy)Cl_2$ was made by a modification of the *Inorganic Syntheses* preparation[3] for 2,2′-iminodipyridinedichlorocobalt(II). An equimolar quantity of

[1] W. W. WENDLANDT, *Texas J. Sci.* **10**, 271 (1958).
[2] N. I. LOBANOV, I. S. RASSONSKAYA and A. V. ABLOV, *Zh. Neorg. Khim.* **3**, 1355 (1958).
[3] J. C. BAILAR, JR. and S. KIRSCHNER, *Inorg. Synth.* **5**, 184 (1957).

2,2′-bipyridine was substituted for the iminodipyridine, and the procedure was carried out as specified in the above reference. The product is a light blue powder. (Found: Co, 20·8; Cl, 25·5. Calc. for $Co(bipy)Cl_2$, Co, 20·6; Cl, 24·8%).

2,2′-*Iminodipyridinedichlorocobalt*(II). $Co(IDP)Cl_2$, was made by the method of BAILAR and KIRSCHNER[3].

(Found: Co, 20·0. Calc. for $Co[NH(C_5H_4N)_2]Cl_2$, Co, 19·6%.)

Hexamminecobalt(III) *chloride*. $[Co(NH_3)_6]Cl_3$ was made according to the procedure given by PALMER[4]. (Found: Co, 22·5; NH_3, 38·9; Cl, 38·7. Calc. for $[Co(NH_3)_6]Cl_3$, Co, 22·0; NH_3, 38·2; Cl, 39·8%.)

cis-*Tetramminedichlorocobalt*(III) *chloride hemihydrate*, cis-$[Co(NH_3)_4Cl_2]Cl\cdot\frac{1}{2}H_2O$. The compound $[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$, made by the method of BRAUER,[5] was treated with concentrated HCl to yield a purple product. Microscopic examination, however, showed that the product contained a large fraction of green crystals mixed with the purple *cis* compound. Rapid extraction of the crude purple product with H_2O resulted in solution of the purple crystals leaving a green residue. Immediate addition of concentrated HCl to the purple filtrate reprecipitated the purple solid. Microscopic examination of this product showed that it contained only a minute fraction of green crystals. (Found: Co, 24·0; Cl, 43·1; NH_3, 27·2. Calc. for $[Co(NH_3)_4Cl_2]Cl\cdot\frac{1}{2}H_2O$, Co, 24·3; Cl, 43·9; NH_3, 28·1%.)

trans-*Tetramminedichlorocobalt*(III) *chloride*. *trans*-$[Co(NH_3)_4Cl_2]Cl$ was made by BRAUER's procedure,[6] and the product was dehydrated by heating at 95°C to constant weight. (Found: Co, 25·5; Cl, 46·5; NH_3, 29·3. Calc. for $[Co(NH_3)_4Cl_2]Cl$, Co, 25·3; Cl, 45·6; NH_3, 29·2%.)

Tetramminephosphatocobalt(III). $Co(NH_3)_4PO_4$ was made by the recently published method of SIEBERT[7]. (Found: Co, 26·5; NH_3, 31·6. Calc. for $Co(NH_3)_4PO_4$, Co, 26·6; NH_3, 30·7%.)

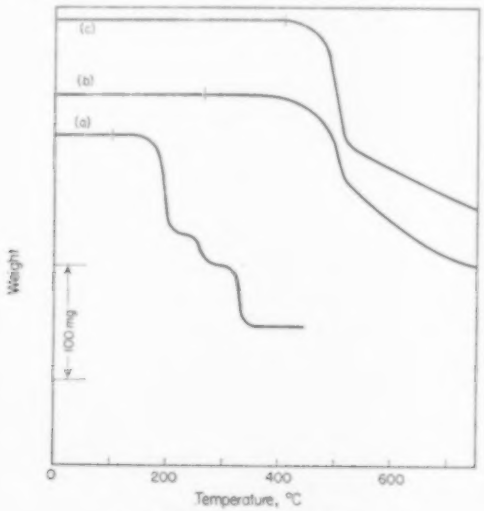

FIG. 1.—Thermogravimetric curves.
Curve (a): $Co(py)_2Cl_2$ (313 mg).
Curve (b): $Co(bipy)Cl_2$ (300 mg).
Curve (c): $Co(IDP)Cl_2$ (313 mg).

RESULTS AND DISCUSSION

Curve 1(a). On being heated, $Co(py)_2Cl_2$ starts to lose an alkaline gas at 102°C, and weight loss increases rapidly as the temperature is raised further. At 233°C there

[4] W. G. PALMER, *Experimental Inorganic Chemistry* p. 530. Cambridge University Press (1954).
[5] G. BRAUER, *Handbuch der Präparativen Anorganischen Chemie* p. 1147. Ferdinand Enke Verlag, Stuttgart (1954).
[6] G. BRAUER, *Handbuch der Präparativen Anorganischen Chemie* p.1148. Ferdinand Enke Verlag, Stuttgart (1954).
[7] H. SIEBERT, *Z. Anorg. Chem.* **296**, 280 (1958).

is a plateau corresponding to the composition, $Co(py)Cl_2$. Evolution of alkaline gas resumes when the temperature is increased until at 284°C there is a well-defined plateau corresponding to the composition $Co_3(py)_2Cl_6$. At a temperature of 370°C $CoCl_2$ is formed as evidenced by the weight of the residue, its blue colour which changes to pink in humid air, and its X-ray diffraction pattern. Only alkaline gases are evolved during the entire heating period.

Curve 1(b). The increased stability due to chelation is demonstrated by a comparison of this curve with curve 1(a). $Co(bipy)Cl_2$ starts to evolve an alkaline gas at 268°C compared to 102°C for the bis(pyridine) compound. With further heating the evolution of the alkaline gas is slow and approximately half of the amine is still present at 540°C. At this temperature there is a decrease in the rate of weight loss, and an acid instead of basic, gas is evolved. This indicates extensive decomposition of the remaining material.

Curve 1(c). The thermogravimetric curve for $Co(IDP)Cl_2$ is similar to that of the bipyridine compound (curve 1b). An alkaline gas is evolved until one-half of the amine is lost. At this point (at approximately 523°C), the rate of weight loss decreases noticeably, and an acid gas is evolved for the remainder of the heating period.

Although the initial decomposition temperature of the iminodipyridine compound is higher, the very slow initial decomposition rate of the bipyridine compound causes the two thermogravimetric curves 1(b) and 1(c) to resemble each other closely. To further compare the thermal stabilities of the bipyridine and iminodipyridine complexes, two isothermal heating experiments were performed—one at 300°C and the other at 350°C. At 300°C $Co(bipy)Cl_2$ loses weight at an initial rate of about 1 per cent/hr. The rate slows down steadily and after 20 hr (at a total weight loss of 11 per cent) further weight loss is extremely slow. Chemical analysis of the final product shows only nitrogen-containing material, but no chlorine, is lost. On the other hand, $Co(IDP)Cl_2$ loses only 0·66 per cent of its weight after 18 hr at 300°C. The relative behaviour of the two compounds is similar at 350°C. At this temperature the bipyridine compound loses weight rapidly at first and then levels off after about 19 hr at a weight loss of 26·5 per cent. The iminodipyridine compound loses 5·25 per cent of its weight after 22 hr at the same temperature. These isothermal comparisons confirm the greater thermal stability of the iminodipyridine compound, but they also demonstrate that decomposition temperatures are dependent upon the method of heating and that thermogravimetric studies done in the usual way, with increasing temperature, can have only relative significance.

Recent investigations[8] of $Co(py)_2Cl_2$ have confirmed the existence of a tetrahedral configuration for cobalt(II). $Co(py)_2Cl_2$ occurs in blue and violet forms with differing magnetic moments. To explain the magnetic moments, MELLOR and CORYELL[9] proposed that the violet form is a polymer of the $(Cd(NH_3)_2Cl_2)_x$ type with edges shared between adjacent octahedra by double chloride bridging. The blue form is monomeric and tetrahedral. The violet form is stable at room temperature, but it is readily converted to the blue form by heating, even at temperatures below 100°C. Since both the iminodipyridine compound and the bipyridine compound are blue, it is probable that they are tetrahedral even at room temperature. Molecular models of

[8a] J. D. DUNITZ, *Acta Cryst.* **10**, 307 (1957); [8b] E. FERRONI and E. BONDI, *J. Inorg. Nucl. Chem.* **8**, 458 (1958).
[9] D. P. MELLOR and C. D. CORYELL, *J. Amer. Chem. Soc.* **60**, 1786 (1938).

Vol. 15 1960

the two amines show that the extra ring member in iminodipyridine allows a better fit of the two co-ordinating nitrogen atoms on the tetrahedral cobalt(II) atom.

The significantly higher stability of the iminodipyridine compound compared to the bipyridine compound is probably a result of the steric advantage of the six-membered ring and, also, the undoubtedly higher basicity of the ring nitrogens in the iminodipyridine. It has been found[10] that methyl substituted derivatives of phenanthroline and bipyridine are more basic than the parent compounds. This effect, which is due to the electron releasing properties of the methyl group enhancing the donor properties of the ring nitrogen, would be expected to be even more significant in the case of amine substitution on the ring.

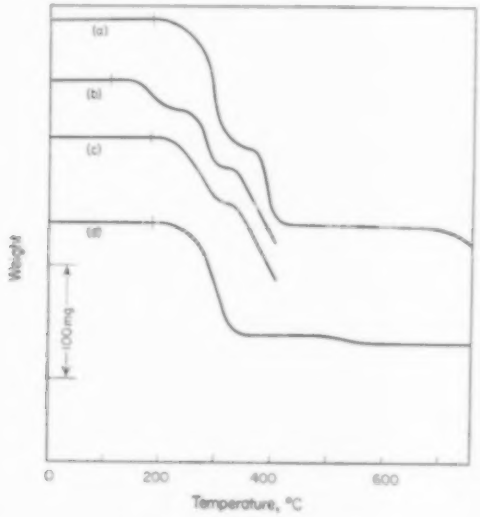

FIG. 2.—Thermogravimetric curves.
Curve (a): $[Co(NH_3)_6]Cl_3$ (353 mg).
Curve (b): *cis*-$[Co(NH_3)_4Cl_2]Cl{\cdot}\frac{1}{2}H_2O$ (300 mg).
Curve (c): *trans*-$[Co(NH_3)_4Cl_2]Cl$ (300 mg).
Curve (d): $Co(NH_3)_4PO_4$ (316 mg).

Curve 2(a). Hexamminecobalt(III) chloride starts to lose ammonia at 184°C. As the temperature is raised, the rate of ammonia evolution increases, but at a composition corresponding to the compound, $Co(NH_3)Cl_3$, and at a temperature of 310°C, there is a significant decrease in the rate of weight loss. When the temperature is further increased to 364°C, the rapid evolution of ammonia resumes. At 435°C the weight corresponds very closely to $CoCl_2$. No further weight decrease is noted until 645°C when there is a slow evolution of an acid gas. At this point the residue is visibly heterogeneous, consisting of black and blue portions. The latter turns pink in moist air, and X-ray diffraction shows it to contain $CoCl_2$.

This thermogravimetric curve does not conform in all details to that determined by WENDLANDT[1]. Using a heating rate of 5·4°C/min with the sample in a slow moving stream of air, WENDLANDT observed a very rapid loss of ammonia starting at 160°C. The weight reached a value corresponding to $CoCl_2$ at 360°C, with only a

[10] M. YASUDA, K. SONE and K. YAMASAKI, *J. Phys. Chem.* **60**, 1667 (1956).

slight change in slope at the midpoint of the curve corresponding to a triammine composition. Above 360°C, oxidation of the $CoCl_2$ probably was the predominant reaction. Both WENDLANDT's and the present work are in fair agreement with previous determinations of the initial decomposition temperature. CLARK, QUICK and HARKINS[11] state that the initial decomposition begins at 173°C, but they add, in agreement with the earlier work of BILTZ[12], that the first step in the decomposition is the formation of the pentamminechlorocobalt(III) chloride. WENDLANDT has found that the pentammine decomposes rapidly after the temperature exceeds 170°C, so that it is not likely that its formation would be observed on heating the hexammine at as high a heating rate as 300°C/hr. The course of the decomposition is probably complex since CLARK *et al.*, observed the formation of NH_4Cl on the walls of the container when the hexammine was heated to 181°C.

LOBANOV and his co-workers report that, under their experimental conditions, differential thermal analysis shows the hexammine to be stable up to 250°C and then to undergo an endothermic effect at 280°C, which they attribute to the loss of one ammonia. They acknowledge previous evidence that hexamminecobalt chloride decomposes well below 200°C and conclude that differential thermal curves will not always indicate processes which take place on slow heating. Since we employed the same heating rate as LOBANOV, our data are complementary. The first large general endothermic effect observed by LOBANOV at 280°C corresponds closely to the start of the maximum rate of ammonia loss on the initial part of our curve (Fig. 2a). The second and smaller endothermic effect they observed corresponds closely to the second period of rapid weight loss on the lower part of our pyrolysis curve. Because we did not observe any indication of the formation of the pentammine, we do not believe that the first endothermic effect is indicative merely of the loss of one ammonia.

Curves 2(b) *and* 2(c). Both *cis*- and *trans*-tetramminedichlorocobalt(III) chloride have similar thermogravimetric curves. The *cis* compound is a hemihydrate and therefore starts to lose weight at a lower temperature than the *trans* compound. After the initial loss of water, starting at 118°C the curves are very similar. In both cases alkaline gases are evolved (starting at 180°C in the case of the *trans* compound) and in both compounds there is a distinct arrest at a weight corresponding to the loss of three molecules of ammonia. This, interestingly, could indicate a tetrahedrally co-ordinated cobalt(III) compound with the formula $Co(NH_3)Cl_3$, but other interpretations are also possible. Further heating converts both compounds to $CoCl_2$ as evidenced by the formation of blue residues which turn pink in moist air and by X-ray diffraction patterns. The thermal similarity of some *cis* and *trans* forms of hexa-co-ordinated cobalt(III) complexes has been noted also by WENDLANDT[1], who discovered a similar thermal behaviour for the *cis* and *trans* forms of $[Co(en)_2Cl_2]Cl$ and by LOBANOV *et al.*[2], who have reached the same conclusion regarding the thermal decomposition of *cis*- and *trans*-tetramminedinitrocobalt(III) nitrate. On the other hand LOBANOV has found differences in the thermal decomposition of the *cis* and *trans* forms of $[Co(en)_2(NH_3)(NO_2)](NO_2)_2$.

Curve 2(d). Tetramminephosphatocobalt(III) starts to lose ammonia at 184°C, and ammonia loss continues at a rapid rate to a temperature of 375°C. There is then a slow weight loss as the temperature is raised higher, and a very weakly alkaline or

[11] G. L. CLARK, A. J. QUICK and W. D. HARKINS, *J. Amer. Chem. Soc.* **42**, 2496 (1920).
[12] W. BILTZ, *Z. Anorg. Chem.* **83**, 177 (1913).

Vol. 15 1960

neutral gas is evolved from the muffle. At 598°C all weight loss ceases, and the weight remains constant up to 760°C. The initial weight of the sample was 316·1 mg, and the residue weighed 206·9 mg indicating the material had been converted to cobaltous pyrophosphate, $Co_2P_2O_7$. Probably all ammonia evolution had stopped at 375°C, and the product at that point was $CoPO_4$. The very weak alkaline gas detected after that point probably remained in the muffle after the initial decomposition and was not swept out by the slow-moving stream of nitrogen.

CONCLUSIONS

1. Increased thermal stability due to chelation has been demonstrated by a thermogravimetric comparison of $Co(py)_2Cl_2$ and $Co(bipy)Cl_2$. Thermal decomposition starts at 102°C. for the former and at 268°C for the latter compound.

2. The somewhat greater thermal stability of the iminodipyridine complex of $CoCl_2$ compared to the analogous bipyridine compound is probably due to the steric advantage of the six-membered chelate ring in complexes of tetrahedral cobalt(II) and also to the higher basicity of the ring nitrogens in the iminodipyridine.

3. Under the conditions employed in this work there is little difference in the thermal response of the *cis* and *trans* forms of $[Co(NH_3)_4Cl_2]Cl$.

4. In general, cobalt(III) ammines are fairly unstable compounds. The salts examined here: $[Co(NH_3)_6]Cl_3$, *cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$ and $Co(NH_3)_4PO_4$ all showed signs of decomposition at about 180°C. It should be noted that this temperature is the point at which these compounds showed measurable decomposition in thermogravimetric analyses when a rather rapid heating rate of 300°C/hr was used. It is, therefore, probable that they will decompose at appreciable rates at even lower temperatures since a rapid heating rate will not detect the inception of slow decomposition.

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SOME NEW BROMINE–AMINE COMPLEXES

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Abstract—Bromine reacts with 2-bromopyridine or 2-chloropyridine to produce an unusual type of amine-halogen complex. Elemental analyses and "free" bromine analyses suggest the formulation $(C_5H_4BrNH)^+Br^-\cdot C_5H_4BrN\cdot Br_2$ and $(C_5H_4ClNH)^+Br^-\cdot C_5H_4ClN\cdot Br_2$. Infra-red studies and preliminary X-ray data support these formulations.

The concentration equilibrium quotient for the system 2-chloropyridine–iodine has also been studied spectrophotometrically. The average value for the association equilibrium quotient of the 1:1 complex has been found to be 3·3 at 28°C.

RECENTLY, ZINGARO and TOLBERG[1] investigated the infra-red spectra of a number of pyridine-co-ordinated iodine(I) salts. They showed that the salts of the type (IPy)X and $(IPy_2)X$ possess infra-red absorption bands in the 1000 cm^{-1} region which correspond to the new bands found in this region for solutions of iodine in pyridine.[2,3,4] This work has been extended[5] recently to include a number of analogous bromine(I) salts, and solutions of halogens and interhalogens in pyridine and a number of substituted pyridines.

During the course of this investigation a new type of bromine–amine complex was isolated which is described. Also, the equilibrium quotient for the iodine–2-chloropyridine system was measured and it is compared with those for the iodine–pyridine and iodine–benzene systems, which have been the subject of numerous recent investigations.

EXPERIMENTAL

2-Bromopyridine. Eastman white label grade 2-bromopyridine was dried over sodium hydroxide for several days and then distilled from calcium oxide at reduced pressure. The fraction having a constant boiling point of 49°C at 2·7 mm was collected. The index of refraction at 20°C was 1·5713.

2-Chloropyridine. Eastman white label 2-chloropyridine was purified in the same way as the bromopyridine. A constant boiling fraction was collected at 49·0°C and 7 mm. This fraction had an index of refraction of 1·5322 at 20°C.

Bromine and iodine. Mallinckrodt "Analytical Reagent" grade bromine and iodine were used without further purification.

n-Hexane. Phillips "Spectra" grade n-hexane was used without further purification.

Chloroform. Mallinckrodt "Analytical Reagent" grade chloroform was used without further purification.

Bromine–amine complexes. Chloroform solutions containing 2-bromopyridine and bromine in various concentrations were allowed to stand in closed flasks. Within 24 hr orange crystals began to separate from those solutions in which the mole ratio of 2-bromopyridine to bromine was 3:1.

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Vol. 15 1960

After five days the crystals were separated by filtration and washed with carbon tetrachloride and a small amount of dry air and the product was analysed.

Orange crystals were obtained from chloroform solution containing 2-chloropyridine and bromine in the manner described above, but several days were required before any crystal formation occurred.

Analyses. The formation of free iodine upon treatment of the complex with aqueous potassium iodide showed that some molecular bromine was associated with the amine. This bromine, hereafter designated as "free" bromine, was determined by treating a weighed sample with excess potassium iodide and a few drops of HCl. The iodine liberated was titrated with standard sodium thiosulphate solution using starch indicator.

TABLE 1.—ANALYTICAL DATA FOR COMPLEX SALTS

Compound		C(%)	H(%)	N(%)	Total halogen(%)	"Free" bromine(%)	Mol. wt.	m.p. (°C)
Reaction product of Br_2 + 2-bromo-pyridine	Experimental	20·88	1·60	4·93	72·05	28·3	575*	87–91 dec.
	Calculated	21·57	1·63	5·03	71·76	28·7†	557	
Reaction product of Br_2 + 2-chloro-pyridine	Experimental	25·87	1·89	6·28	65·00	34·1	482*	74–83 dec.
	Calculated	25·67	1·94	6·00	66·40	34·2†	468	

* These molecular weights result from X-ray crystal studies[6] and are based on the assumption that the molar weight of a unit cell is twice the molecular weight of the compound. The observed space group ($P\bar{1}$) is consistent with a structure containing two molecular entities per unit cell. X-ray studies also show that the two compounds are isomorphous.

† Calculated from subsequently proposed formulation.

Complete elemental analyses were performed by a commercial laboratory.‡

Solutions for equilibrium study. A standard iodine solution in n-hexane was prepared, and other solutions were made by dilution of the standard stock solution.

A standard solution of 2-chloropyridine was prepared by weighing out a sample from a weight burette and diluting to volume with n-hexane.

Apparatus. A Beckman IR-4 spectrometer was used for the infra-red studies and a Beckman DK-1 was used for the equilibrium measurements.

RESULTS AND DISCUSSION

Complex salts. The results of elemental analyses and X-ray crystal studies§ suggest the empirical formulae $C_{10}H_9N_2Br_5$ and $C_{10}H_9N_2Cl_2Br_3$ for the 2-bromo-pyridine–bromine and 2-chloropyridine–bromine compounds, respectively. The experimental data and the corresponding values calculated for the proposed empirical formulas are given in Table 1.

The proposed empirical formula, together with the "free" bromine content suggest that these molecular entities are composed of one molecule of 2-halopyridinium bromide coupled with one molecule of a 2-halopyridine–bromine complex. Without implying anything about the structure, such aggregates could be represented as $(C_5H_4XNH)^+Br^-\cdot C_5H_4XNBr_2$, where X is the ring substituted chlorine or bromine.

The infra-red spectra of these compounds corroborate the proposed formulation. ZINGARO and TOLBERG[1] have shown that the 990 cm^{-1} absorption band of pyridine is replaced by a new intense band at higher frequencies in a number of pyridine-co-ordinated iodine(I) salts. A similar phenomenon has been observed for pyridine-co-ordinated and substituted pyridine-co-ordinated bromine(I) salts.[5] This absorption

‡ Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

§ Complete single crystal X-ray analyses of these compounds is being undertaken in this department.[6]

[6] E. A. MEYERS. To be published.

shift has been interpreted by ZINGARO and TOLBERG as evidence for an interaction between the halogen and the nitrogen of the pyridine ring.

Figs. 1 and 2 indicate that an interaction of the same type occurs in the complex salts reported here. The 988 cm^{-1} band of 2-bromopyridine disappears (Fig. 1) and a

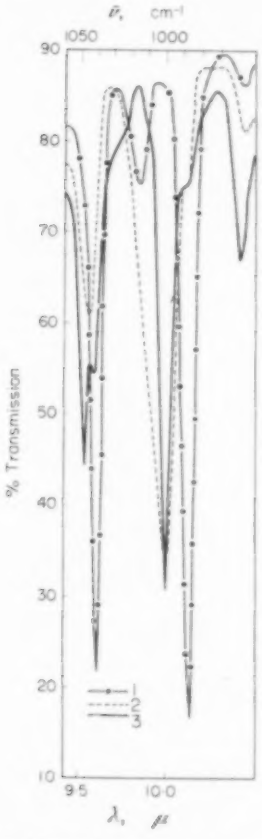

FIG. 1.—Infra-red absorption spectra of (1) chloroform solution, 1·0 F in 2-bromopyridine, (2) chloroform solution 1·0 F in 2-bromopyridine and 4·0 F in bromine, and (3) solid $(C_5H_4BrNH)^+Br^-{\cdot}C_5H_4BrN{\cdot}Br_2$ in KBr.

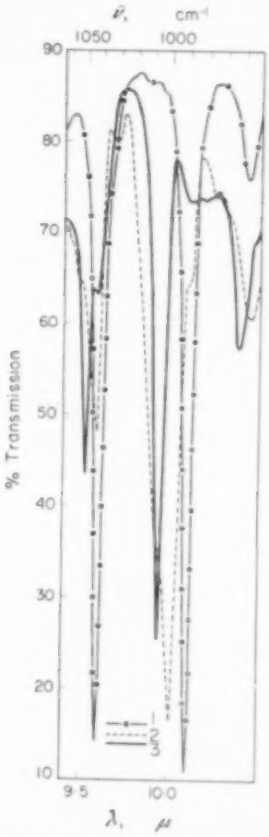

FIG. 2.—Infra-red absorption spectra of (1) chloroform solution, 1·0 F in 2-chloropyridine, (2) chloroform solution 1·0 F in 2-chloropyridine and 4·0 F in bromine, and (3) solid $(C_5H_4ClNH)^+Br^-{\cdot}C_5H_4ClN{\cdot}Br_2$ in KBr.

new intense band appears at 1000 cm^{-1} in a freshly prepared 1·0 F 2-bromopyridine solution in chloroform containing a fourfold excess of bromine. In view of the subsequent results obtained in the iodine–2-chloropyridine equilibrium study, this band probably corresponds to the 1 : 1 complex formed between 2-bromopyridine and bromine. The fact that the complex salt, $(C_5H_4BrNH)^+Br^-{\cdot}C_5H_4BrN{\cdot}Br_2$ is characterized by an intense absorption band at 1000 cm^{-1} indicates that Br_2 is complexed in a manner similar to that in the 1 : 1 bromine–2-bromopyridine complex.

Fig. 2 shows that similar reasoning may be applied to the complex salt formed with 2-chloropyridine. The intense band at 991 cm^{-1} observed for 2-chloropyridine is

Vol. 15 1960

replaced by a new intense band at 1002 cm^{-1} in a fresh solution containing 2-chloropyridine and excess bromine. The complex salt, $(C_5H_4ClNH)^+Br^-\cdot C_5H_4ClN\cdot Br_2$ has an intense absorption band at 1006 cm^{-1}.

The complex salts form readily in chloroform, but only very slowly in carbon tetrachloride. In fact, the (2-chloropyridine)$_2$·HBr·Br_2 does not form in carbon tetrachloride, even after several months. These observations suggest that the bromination of chloroform is involved. The HBr produced during bromination could then react with free base to form the 2-halopyridinium bromide. This molecular entity could then combine with a molecule of 2-halopyridine–bromine complex, forming the complex salt.

An alternative source of HBr would involve halogenation of the 2-halopyridine, and this is probably the case for the formation of the salts in carbon tetrachloride. Evidence of such a possibility has been reported.[7] The mechanism of formation of these complex molecules requires further study.

Equilibrium study. A spectroscopic study of the 2-chloropyridine–iodine system was made in order to learn something of the type of complex involved and its equilibrium quotient. Iodine was chosen instead of bromine since bromine was found to react with hexane, and since comparable data for the pyridine–iodine[8,9] and benzene–iodine[10] systems are available for comparison.

Absorbance measurements in n-hexane solutions showed an absorption maximum for iodine at 517 mμ with a molar extinction coefficient, ε,* of 920.

In order to study the absorption of the complex, the formal concentration of iodine was maintained at a constant value and the 2-chloropyridine (hereafter called "CP") concentration was varied. A plot of absorbance versus the CP to I_2 mole ratio showed that essentially all of the iodine is complexed when the mole ratio reaches 6000 : 1, and the absorption maximum of this solution is located at 436 mμ. The molar extinction coefficients for the complex at 436 mμ and 517 mμ are, 1190 and 213, respectively, and the molar extinction coefficient of iodine at 436 mμ is 50.

The iodine concentration at various mole ratios was determined by solving the simultaneous equations:

$$A_{517} = \varepsilon_{c,517}[C] + \varepsilon_{I_2,517}[I_2]$$
$$A_{436} = \varepsilon_{c,436}[C] + \varepsilon_{I_2,436}[I_2]$$

where A_{517} is the total absorbance at 517 mμ, $\varepsilon_{c,517}$ is the molar extinction coefficient of the complex at 517 mμ, [C] is the concentration of the complex, etc.

Assuming the formation of a 1 : 1 complex, the concentration equilibrium quotient ($K = [CP\cdot I_2]/[CP][I_2]$) was then calculated. The data and results are summarized in Table 2. Available data[9,10] for the pyridine–iodine and benzene iodine complexes are: Py·I_2—$\lambda_{max} = 406$ mμ, $K = 101$ at 25°C; Bz·I_2—$\lambda_{max} = 500$ mμ, $K = 1{\cdot}72$ at 25°C.

Comparison of these values with that obtained suggests the following conclusions. First, the relative constancy of the equilibrium quotients supports the assumed

* $$\varepsilon = \frac{\text{absorbance}}{[I_2]\,(\text{sample path length})}$$

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TABLE 2.—ABSORPTION CHARACTERISTICS AND EQUILIBRIUM QUOTIENTS FOR THE 2-CHLOROPYRIDINE–IODINE COMPLEX IN n-HEXANE AT 28°C

Formal mole ratio $\frac{[CP]^*}{[I_2]}$	A_{517}	A_{436}	$K = \frac{[CP{\cdot}I_2]}{[CP][I_2]}$
0	0·528	0·036	—
42·1	0·499	0·069	3·0
84·2	0·468	0·102	3·3
175	0·423	0·164	3·3
365	0·358	0·268	3·8
536	0·320	0·306	3·2
730	0·283	0·370	3·4
921	0·265	0·418	3·3
1500	0·241	0·516	3·0
5930	0·122	0·683	—
			Av. 3·3

* The initial concentration of iodine in each case was $5{\cdot}73 \times 10^{-4}$ M.

formation of 1 : 1 complex. Second, the value of the equilibrium quotient for the $CP{\cdot}I_2$ complex indicates that 2-chloropyridine forms a more stable complex than benzene, but one considerably less stable than that formed with pyridine. This follows exactly in the order that would have been predicted on the basis of their relative basic strengths. Also, the assumption that all of the iodine is complexed at a CP to I_2 mole ratio of about 6000 : 1 is justified.

Vol. 15 1960

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THE SILYL GROUP AS AN ELECTRON ACCEPTOR—III

THE RELATIVE STABILITIES OF SOME COMPLEXES OF SILYL IODIDE WITH ETHERS AND THIOETHERS

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Abstract—Vapour-pressure measurements were carried out at low temperatures with mixtures of silyl iodide, SiH_3I, and the following Group VI donor molecules—Me_2O, Me_2S, furan, thiophen, tetrahydrofuran and tetrahydrothiophen. From these measurements, the stoicheiometry and relative stability of the complexes are inferred. Unlike borine or trimethylboron, silyl iodide forms a moderately strong complex only with tetrahydrofuran.

A RECENT classification has shown[1] that there are two broad classes into which elements can be placed, on the basis of their behaviour towards electron-donating ligands. Elements of Class (*a*), such as aluminium, form complexes whose stability decreases in the order: N > P > As > Sb, while complexes formed from elements of Class (*b*), for example platinum, typically show an order of stability such as: N ≪ P > As > Sb. Some elements show each type of behaviour in different compounds; in particular, boron, which normally exhibits Class (*a*) behaviour, can show weak Class (*b*) characteristics in complexes of borine or trimethylboron with Group VI donors.[2,3] The purpose of this investigation was to see if silicon hydride derivatives, which are often similar in their chemistry to boron hydride derivatives, might show this mixed (*a*) and (*b*) character.

Those adducts that have been reported between Group V donors and silicon hydrides and their derivatives, and a selection of those involving silicon tetrahalides, are shown in Table 1.

It may be noted that the presence of at least one silicon–halogen bond is necessary for complex formation, and also that the donor molecules used were rather similar in type. The results with phosphorus and arsenic compounds indicate Class (*a*) behaviour. There is no general agreement on the nature of these adducts; some, e.g. $SiH_3X.NMe_3$, have been formulated as quaternary compounds,[7,14] and conductivity data seem to

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TABLE 1

Compound	Ligand	Ratio (C : L)	Remarks	Reference
SiH_4	NMe_3	—	no adducts reported	4
$SiHF_3$	NMe_3	1 : 1		5
SiF_4	NMe_3	1 : 1, 1 : 2		5, 6
SiH_3Cl	NMe_3	1 : 1		4, 7
SiH_2Cl_2	NMe_3	1 : 1	decreasing stability	4
$SiHCl_3$	NMe_3	1 : 1		4
$SiCl_4$	NMe_3	1 : 1		4
$SiCl_4$	NC_5H_5	1 : 2		8, 9
SiH_3Br	$PHMe_2$	1 : 1	v. unstable	10
$SiBr_4$	NC_5H_5	1 : 2		8, 11
SiH_3I	NMe_3	1 : 1, 1 : 2	decreasing stability	12
SiH_3I	PMe_3	1 : 1		12
SiH_3I	$AsMe_3$	1 : 1		12
SiH_3I	N_2Me_4	1 : 1, 2 : 1		13
SiI_4	NC_5H_5	1 : 4		8

support this view.[12] On the other hand, STONE and SEYFERTH[15] consider them to be compounds of five-co-ordinate silicon, while FERGUSSON *et al.*[16] have recently suggested that some, e.g. $SiHF_3.NMe_3$, may be halogen-bridged six-co-ordinate dimers.

Group VI ligands usually form weaker complexes that are more sensitive to changes in co-ordination type. Little has been reported concerning silicon compounds, and much of the evidence is negative or ambiguous. Freezing point and dipole moment studies have shown that silicon tetrachloride forms no complexes with diethyl ether, tetrahydrofuran and dioxan,[17,18] and this has been attributed to a steric effect;[19] the existence of weak adducts with anisole and phenetole[20] seems to throw doubt on this conclusion, however. Silicochloroform forms a weak adduct with tetrahydrofuran, but none with diethyl ether,[21] while silicon tetrabromide gives a 1:4 complex with dioxan;[18] it has been suggested[14] that, in this last compound, bromine atoms are acting as acceptors. No adduct was formed in the reaction between thiophen and silicon tetrachloride.[8] Finally, a liquid phase reaction between silyl iodide and dimethyl sulphide was observed to yield no solid product,[22] showing that no stable sulphonium compound was formed under those conditions.

Further indirect evidence is provided by observations on the difficulty of separating silyl compounds from diethyl ether:[23,24] in the case of a series of monoalkyl silanes, an adduct was postulated, but no evidence could be found for it from infra-red studies or from vapour–liquid equilibrium measurements. The easy hydrolysis of many silicon

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Vol. 15 1960

compounds has often been attributed[15] to initial co-ordination of OH^-, and kinetic studies have been interpreted on this basis,[25] although it has been pointed out that an S_N2 mechanism is also consistent with the facts.[26,27] Recent work by SOMMER, however, appears to favour the hypothesis of a five-covalent intermediate.[28]

Silyl iodide was chosen for these experiments both because it is known to give stable adducts with Group V donor molecules,[12] and because it has low steric requirements coupled with convenient volatility. It was prepared either by the iodination of silane or by a new route, more suitable for large-scale preparations, involving the cleavage of chlorophenysilane[29,30] by hydrogen iodide.[31,32,33a]

EXPERIMENTAL

Technique

All manipulations of volatile compounds were carried out in a mercury-free high vacuum apparatus; involatile liquids and solids were handled in a nitrogen-filled drybox. For experiments 1(a), (b) and 2, low temperatures were maintained in the cryostat already described,[24] and were accurate to better than ±0·1°C above −80°C.† Vapour pressures were measured by means of a modified type of spoon gauge[23b] accurate to ±0·05 mm, while a Hilger H800 spectrometer was used for the infrared measurements.

Materials

Silyl iodide was fractionated *in vacuo* until homogeneous (Found: M, 158. Calc. for SiH_3I; 157·9. Vapour pressure: 12·3 cm/0°; lit.,[34] 12·39 cm, m.p., −56° ± 2°; lit.,[34] −57°). Donor molecules were dried and fractionated *in vacuo* as shown below—

Compound	Dried with	Held at	Passed through
$(CH_3)_2O$	Na/K	−140°C	−96°C
$(CH_3)_2S$	$CaSO_4$, then Na	—*	—
C_4H_4O	$CaSO_4$, then $LiAlH_4$	−96	−84
C_4H_4S	$LiAlH_4$	−84	−46
C_4H_8O	$CaSO_4$, then $LiAlH_4$	−96	−64
C_4H_8S	$CaSO_4$, then $LiAlH_4$	−64	−23

* Fractionated in a low-temperature column (b.p., −20·1°/5·1 cm).

A middle fraction was then taken from each sample, and checked tensimetrically for homogeneity.

Vapour-pressure Measurements

1. *System: silyl iodide–dimethyl ether*

For dimethyl ether alone, values agreed with those given by KENNEDY *et al.*[35] Fig. 1 shows values obtained from mixtures containing 50 mole per cent [runs 1(a) and (b)] and 53·3 mole per cent silyl

† For the other experiments, constant-temperature slush baths were used.

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[34] B. J. AYLETT, *J. Chem. Soc.* 4152 (1957).
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iodide [run 1(c)]. While points along the bottom line represented a reversible change, other points did not; this is shown by the arrows.

The infra-red absorption spectrum of a mixture containing 50·0 mole per cent of silyl iodide was examined; it was essentially a superposition of the separate spectra. The mixture was allowed to stand at −27·3° for 1 hr (vapour pressure ~ 32 cm) and then re-examined under the same conditions. A slight decrease in the relative intensity of the ether absorption was noticed, possibly due to trapping of the ether in tap grease. The only other change was that in the contour of the Si-H bending frequency absorptions and was consistent with slight disproportionation of the silyl iodide.

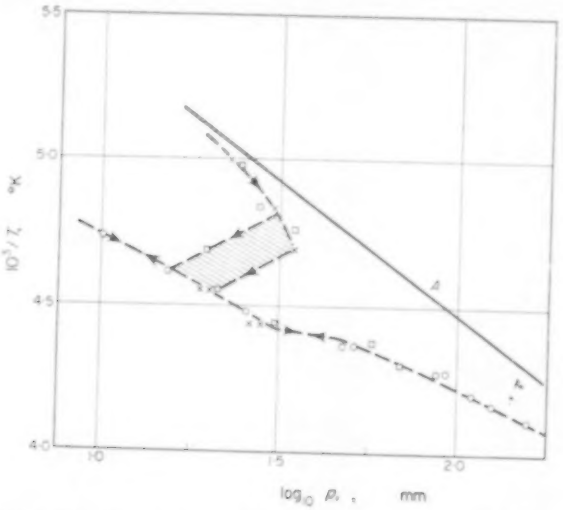

FIG. 1.—Silyl iodide–dimethyl ether, from −73 to −30°C × run 1(a), □ run 1(b), ○ run 1(c). A, sum of partial pressures for 50 mole per cent silyl iodide. Shaded area represents non-equilibrium region.

2. *System: silyl iodide–dimethyl sulphide*

For dimethyl sulphide alone (compare ref. 36):—

T°C	−72·5	−66·2	−59·8	−53·7	−44·7	−35·8	−27·3	−20·1	−13·4	0
p(mm)	1·0	1·7	3·5	6·2	12·1	22·3	38·9	58·2	85·5	168·0

Representative data for mixtures are given in Figs. 2 and 3.* After remaining at room temperature for 1 hr, a mixture containing 19·3 mole % silyl iodide had increased its vapour pressure at −59·8° from 3·0 mm to 7·5 mm, hence some reaction had occurred. No solid products were observed either then or at any time during the experiments.

3. *System: silyl iodide–furan*

Results are shown in Fig. 4. At −46°, a reddish colour developed within a few minutes in the liquid, and after 1 hr, some brown resinous material had formed; the vapour pressure was almost unchanged, however. In a check experiment, 0·1870 g of silyl iodide and 0·1627 g of furan were allowed to stand at room temperature for 20 min, and the volatile materials then recovered. The weight of brown solid was found by difference to be 0·027 g. No silane was formed and the vapour pressure of the mixture was unchanged.

4. *System: silyl iodide–thiophen*

Representative results are shown in Fig. 4. The mixtures were liquid above −70°C, and readily

* Duplicated lists giving more extensive results may be had on application to the author.

[36] N. DAVIDSON and H. C. BROWN, *J. Amer. Chem. Soc.* **64**, 316 (1942); D. W. OSBORNE, R. N. DOESCHER and D. M. YOST, *Ibid.* **64**, 169 (1942).

Vol. 15 1960

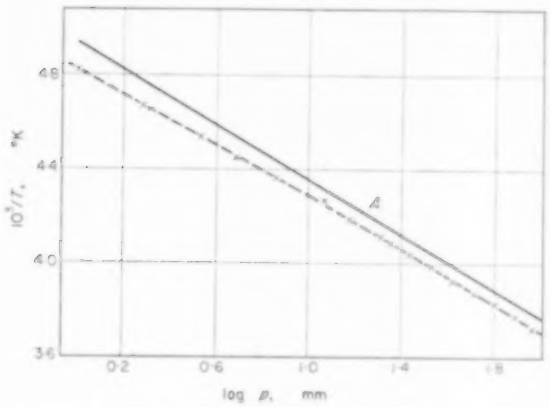

FIG. 2.—Silyl iodide–dimethyl sulphide, from −72 to −6°C, with 50 mole per cent silyl iodide. *A*, sum of partial pressures for this mixture.

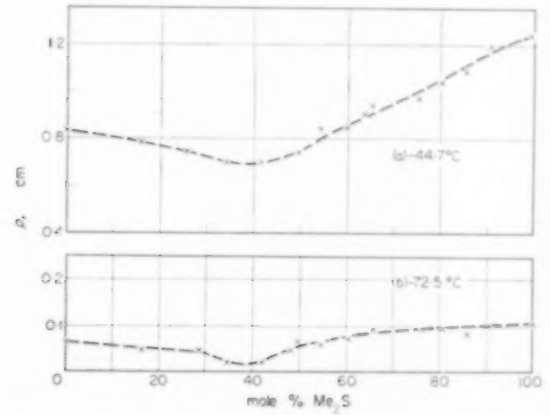

FIG. 3.—Silyl iodide–dimethyl sulphide, in varying mixtures at two fixed temperatures.

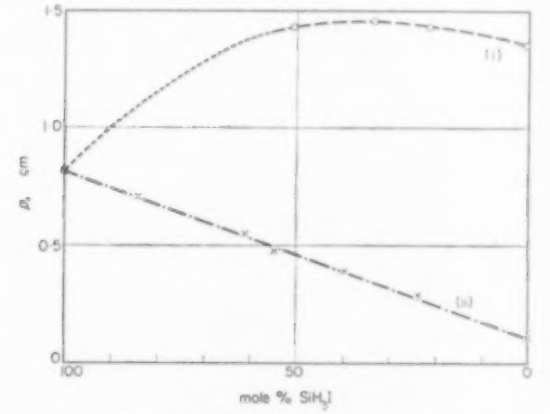

FIG. 4.—Silyl iodide–furan: – – – – –
Silyl iodide–thiophen: – · – · – · –

distilled out of a bath at −46°; after standing at room temperature for 1 hr, the vapour pressure of a typical mixture (54·5% SiH_3I) at 0°C was unchanged.

5. *System: silyl iodide–tetrahydrofuran*

Initial experiments showed that reaction occurred above −46° or when attempts were made to distil a mixture of the two compounds *in vacuo*. Next, the two compounds were condensed successively in a tube at −196°: the mixture, containing 40·8 mole % SiH_3I, yielded the following results.

T°C	−46	−46	−46	−23	−23	0	−23	−46
Time(hr)	0	1	4	0	4	—	—	—
p(mm)	5	2	2·5*	5	70	121·5*	116·5*	111·5*

* Denotes an equilibrium value.

Examination of volatile products showed that none of the silyl iodide taken (0·0691 g) was present, but 0·0070 g of silane were formed (mole ratio $SiH_3I : SiH_4 = 2{\cdot}0 : 1$).

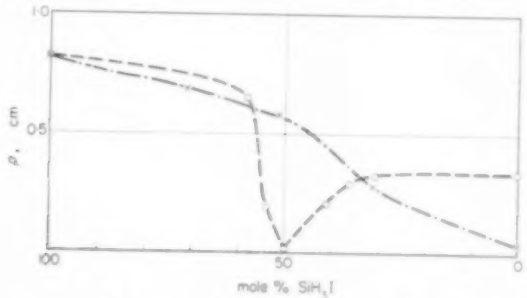

FIG. 5.—Silyl iodide–tetrahydrofuran: – – – – –
Silyl iodide–tetrahydrothiophen: – · – · – · – · –

There remained excess tetrahydrofuran and 0·0780 g of a liquid (vapour pressure < 0·5 mm/20°) (calc. weight for $SiH_3I_2C_4H_8O$: 0·0779 g). The liquid was hydrolysed (NaOH solution) with evolution of hydrogen, and iodine determined (AgI precipitation); results were low unless the hydrolysate was treated with conc. HNO_3 for 12 hr before precipitation.

Equilibrium pressures of mixtures not allowed at any time to warm above −46° are shown in Fig. 5. From a mixture of 0·2118 g of silyl iodide and 0·2214 g tetrahydrofuran held at −46°, 0·1204 g of the latter were removed by pumping (combining ratio, $SiH_3I : C_4H_8O = 1 : 1{\cdot}04$). The solid white adduct was then allowed to warm slowly to room temperature; the vapour pressure remained < 0·5 mm until about −5°, when the solid melted and bubbled violently. The pressure increased rapidly and a colourless liquid was formed. When equilibrium had been reached at room temperature the gas was examined (mole ratio of SiH_3I used to SiH_4 produced, 1·96 : 1). The remaining involatile liquid dissolved readily in diethyl ether; with aqueous silver nitrate solution, the ether solution evolved gas bubbles and deposited a silver mirror. When a little triethylamine was added to the ether solution, gas was evolved, and a white precipitate formed. On heating, the white curdy solid became yellow, then brown, giving off basic fumes. The brown solid was unaffected by water, ether and chloroform, although it dissolved in acetone. When exposed to air, the ether solution slowly formed a white crust and evolved gas. Infra-red examination of the vapour of the involatile liquid (in a 50 cm cell) showed that the absorption differed from that obtained by superimposing spectra of silylene iodide[24,37] and tetrahydrofuran.[38] It resembled more closely the spectra of $Cl_xSi(OMe)_{4-x}$[39] and $Me_2Si(OBu)_2$.[40]

[37] H. J. EMELÉUS, A. G. MACDIARMID and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **1**, 194 (1955).
[38] G. M. BARROW and S. SEARLES, *J. Amer. Chem. Soc.* **75**, 1175 (1953).
[39] R. FORNERIS and E. FUNCK, *Z. Elektrochem.* **62**, 1130 (1958).
[40] R. E. RICHARDS and H. W. THOMPSON, *J. Chem. Soc.* 124 (1949).

Vol. 15 1960

6. *System: silyl iodide–tetrahydrothiophen*

Representative results are shown in Fig. 5. At −23° and above, very slight gas evolution was noted; all the mixtures readily distilled out of a trap at −23°, and could be pumped out of one at −46°. No solid residues were observed.

In another experiment, a mixture containing 52·0 mole per cent silyl iodide was sealed in a small tube and allowed to warm to room temperature. Slight gas evolution was observed, while the liquid was yellow in colour. After heating at 100° for 30 min, no silane was present, neither was there any solid present: the only product appeared to be a colourless liquid of low volatility which was not further examined.

7. *Vapour pressure of silyl iodide*

This had not previously been reported in the range below −23°C.

T°C	−72·5	−66·2	−59·8	−53·7	−44·7	−33·8	−27·3
p(mm)	0·6	1·2	2·2	4·1	8·3	15·9	27·9

DISCUSSION

From Fig. 1, it can be seen that dimethyl ether forms only a weak complex with silyl iodide, and that, when the two reactants are warmed up together from a sufficiently low temperature, reaction occurs at about −60°, near the melting point of silyl iodide. Above about −30°, disproportionation of the silyl iodide occurs slowly, but there is no evidence that further reaction occurs to yield Si—O bonds. Dimethyl ether is known to form a number of quite stable adducts with compounds of elements in Groups II and III such as dimethyl beryllium,[41] diborane[42] and aluminium halides,[43] also with zirconium tetrachloride,[44] and it is rather surprising that interaction with silicon compounds is so weak.

The experiments with dimethyl sulphide were the most critical and were performed in the greatest detail. As can be seen from both methods of presentation (Figs. 2 and 3) there is no evidence for any specific interaction between this compound and silyl iodide. This is in contrast to its behaviour with transition metal compounds[45] and with compounds of elements in Groups II and III, where fairly stable complexes are common. In particular, some transition metal complexes and complexes of borine, BH_3,[2,3] trimethylboron,[3] and diboron tetrachloride[46] are more stable than those with dimethyl ether.

The corresponding pair of heterocyclic compounds, furan and thiophen, both have weak donor properties[47] where σ-bond formation is concerned. There is the possibility, however, that overlap of the π-system of the heterocycle with suitable vacant *d*-orbitals might produce a stronger bond. The known complex $C_4H_4S.VCl_4$[48] may be of this type. From Fig. 4 it appears that, despite this possibility, no adduct is formed between silyl iodide and either of these compounds.

The most clear-cut example of complex formation is afforded by tetrahydrofuran (Fig. 5), which normally is a more efficient donor than dimethyl ether.[49] The 1 : 1

[41] G. E. Coates, F. Glockling and N. D. Huck, *J. Chem. Soc.* 4496 (1952).
[42] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.* **60**, 296 (1938).
[43] R. E. Van Dyke and H. E. Crawford, *J. Amer. Chem. Soc.* **72**, 2829 (1950).
[44] G. Rossmy and H. Stamm, *Liebigs Ann.* **618**, 59 (1958).
[45] e.g. J. Chatt and L. M. Venanzi, *J. Chem. Soc.* 2787 (1955).
[46] T. Wartik and E. F. Apple, *J. Amer. Chem. Soc.* **80**, 6155 (1958).
[47] B. Bak, *Acta Chem. Scand.* **9**, 1355 (1955).
[48] D. Cozzi and S. Cecconi, *Ric. Sci.* **23**, 609 (1953).
[49] H. C. Brown and M. Gerstein, *J. Amer. Chem. Soc.* **72**, 2926 (1950); B. Rice, J. A. Livasy and G. W. Schaeffer, *Ibid.* **77**, 2750 (1955).

solid formed at low temperatures decomposes slowly above $-30°$ in a disproportionation reaction, as has been observed before when Si—H compounds form complexes of medium strength.[7,50] The quantity of silane evolved gives a measure of the extent of disproportionation; at room temperature, equilibrium is soon reached when the mole ratio of silyl iodide used to silane evolved is 2 : 1. This implies that the reaction does not proceed beyond the stage:

$$2SiH_3I \rightarrow SiH_2I_2 + SiH_4$$

since more highly iodinated products would require more silane to be formed. Possibly steric factors involving the reaction complex are unfavourable to such products and prevent further disproportionation.

The involatile liquid that remains after pumping has the composition $SiH_2I_2.C_4H_8O$, but it is suggested that ring cleavage occurs readily to yield $H_2SiI(OCH_2CH_2CH_2CH_2I)$. Such cleavage has been reported, although under more severe conditions, for mixtures of tetrahydrofuran with boron trichloride,[51] silicon tetrachloride,[52] or dimethyldibromosilane;[53] these examples either involve the breaking of strong B—Cl and Si—Cl bonds or are sterically unfavourable, but the fission of weak Si—I bonds should be much easier. This hypothesis would account both for the infrared evidence and for the difficulty in precipitating all the iodine as silver iodide. No doubt once a silicon–oxygen bond has been formed, further complexing of tetrahydrofuran is negligible; silicon compounds in which intramolecular dative π-bonding occurs have much reduced electron-acceptor properties.[54]

Tetrahydrothiophen is known to form a variety of adducts,[55] and it might be predicted, by analogy with tetrahydrofuran and dimethyl ether, that it is a stronger donor than dimethyl sulphide. Recent work by COYLE *et al.*[56], however, shows that, with borine and boron trifluoride, dimethyl sulphide forms the strongest complexes. With silyl iodide, there was no evidence for any interaction with tetrahydrothiophen (Fig. 5); it is known that the C—S bond in complexes such as $(n\text{-}Bu)_2S.BCl_3$[57] is harder to break than is the C—O bond in the corresponding ether complex, and possibly this prevents a reaction similar to that observed with tetrahydrofuran.

Taken together, the results indicate that the order of donor strength is: $(CH_3)_2O > (CH_3)_2S$ and $(CH_2)_4O > (CH_2)_4S$, also that $(CH_2)_4O > (CH_3)_2O$. There is no evidence that silicon in this case displays anything but Class (*a*) character or that it can form complexes with heterocyclic systems.

[50] D. L. BAILEY and G. H. WAGNER, U.S. Pat. 2 732 280; D. L. BAILEY, P. W. SHAFER and G. H. WAGNER, U.S. Pat. 2 732 282.
[51] J. D. EDWARDS, W. GERRARD and M. F. LAPPERT, *J. Chem. Soc.* 1470 (1955).
[52] N. I. SHUĬKIN and I. F. BEL'SKIĬ, *Dokl. Akad. Nauk SSSR* **113**, 366 (1957).
[53] M. KUMADA and H. HATTORI, *J. Inst. Polytech., Osaka City Univ.* **3**, 77 (1952); *J. Chem. Soc. Japan, Industr. Chem. Sect.* **55**, 373 (1952).
[54] B. J. AYLETT, *J. Inorg. Nucl. Chem.* **2**, 325 (1956).
[55] e.g. E. V. WHITEHEAD, R. A. DEAN and F. A. FIDLER, *J. Amer. Chem. Soc.* **73**, 3632 (1951).
[56] T. D. COYLE, H. D. KAESZ and F. G. A. STONE, Abstracts of the Meeting of the American Chemical Society, April, 1959, p. 26 M.
[57] M. F. LAPPERT, *J. Chem. Soc.* 2784 (1953).
[58] H. J. EMELÉUS, A. G. MADDOCK and C. REID, *J. Chem. Soc.* 353 (1941).

Vol. 15 1960

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THE SALTS OF ORGANIC PHOSPHORUS ACIDS—II[1]

THE INFRA-RED SPECTRA OF SALTS OF DI-ALKYL PHOSPHITES

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(*Received* 28 *October* 1958)

Abstract—The infra-red spectra of the sodium, magnesium, silver and mercury salts of a number of di-alkyl phosphites have been recorded and correlated with structural changes imposed upon the di-alkyl phosphite anion by the metal ion present.

As a result of parachor measurements, Raman spectra, infra-red spectra, nuclear magnetic resonance measurements and general chemical properties, the di-alkyl phosphites are best represented by a keto form which exists in the form of dimers or trimers by virtue of hydrogen bonding. X-ray studies[2] indicate that the silver derivatives appear to have the enol structure with an –O–Ag linkage whilst the sodium derivatives are in the keto state with the sodium being bound to phosphorus. Recent studies[3] have indicated that in certain organic solvents the sodium derivatives exist as agglomerates of high molecular weight, which have been formulated by ISBELL as long chain polymers, where the sodium is primarily ionic though possibly exhibiting some *s–p* bonding. By analogy with the mercuration of reactive methylene compounds FOX and VENESKY[4] undertook the mercuration of the di-alkyl phosphites. The structure of the resulting products was regarded as that of a di-alkoxyphosphinyl mercuric acetate with the mercury atom bonded to the phosphorus, rather than the tautomeric form which was expected to be formed from the di-alkyl phosphites.

The infra-red spectra of the salts of the di-alkyl phosphates have previously been studied[1] in an attempt to formulate the interaction between the metal ion and the groups of the di-alkyl phosphate ion, and the present study was undertaken to establish structural changes in the di-alkyl phosphites on salt formation.

EXPERIMENTAL

All solvents were carefully dried. The sodium derivatives[5] of di-methyl, di-ethyl, di-isopropyl and di-n-butyl phosphites were prepared from the appropriate sodium alkoxide and di-alkyl phosphite in solutions of the original alcohols. The products were purified by recrystallisation from the appropriate alcohol–ether solutions. The magnesium derivative of di-ethyl phosphite was obtained[6] from magnesium metal and di-ethyl phosphite containing a slight excess of pyridine, and crystallized from solution on addition of di-ethyl ether.

The silver salts of di-ethyl phosphite[7] were prepared by treating an aqueous solution of di-ethyl phosphite with a few drops of ammonium hydroxide, followed by slow addition of the theoretical amount of silver nitrate solution. The copious precipitate was washed thoroughly with distilled water.

[1] Part I: T. D. SMITH, *J. Inorg. Nucl. Chem.* **9**, 150 (1959).
[2] O. STELLING, *Z. Physik. Chem.* **117**, 161, 194 (1925).
[3] J. R. VAN WAZER, *Phosphorus and its Compounds* Vol. 1, p. 382. Interscience, New York (1958).
[4] R. B. FOX and D. L. VENESKY, *J. Amer. Chem. Soc.* **75**, 3967 (1953).
[5] R. NYLEN, *Ber. Dtsch. Chem. Ges.* **59**, 1119 (1926).
[6] T. MILOBENDZKI and T. KNOLL, *Chem. Polsk.* **15**, 79 (1917).
[7] A. E. ARBUZOV, *Trudy Sessii Akad. Nauk. SSSR, Otdel. Org. Khim.* 211 (1939).

The mercuric acetate and mercuric chloride derivatives of di-ethyl and di-isopropyl phosphites were prepared as described by FOX and VENESKY[4].

The sodium salts of mono-methyl and mono-isopropyl phosphite were prepared by hydrolysis of the respective sodium di-alkyl phosphite in the appropriate alcohol containing one mole of water.

The composition of each product was checked by analysis for carbon, hydrogen and phosphorus. The infra-red spectra were recorded using solid samples ground to form Nujol mulls, using a Grubb–Parsons double-beam recording spectrophotometer.

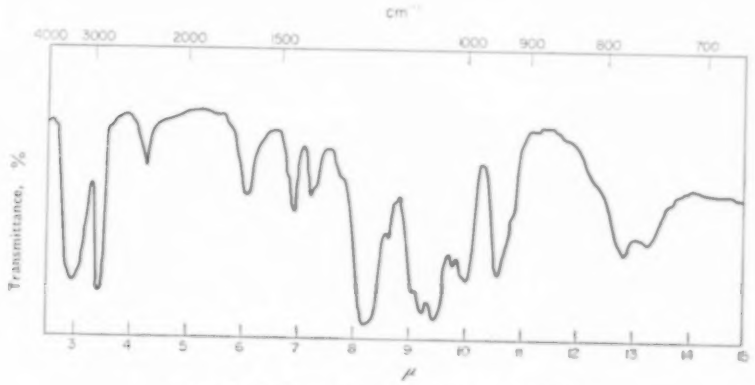

FIG. 1.—Sodium derivative of di-ethyl phosphite.

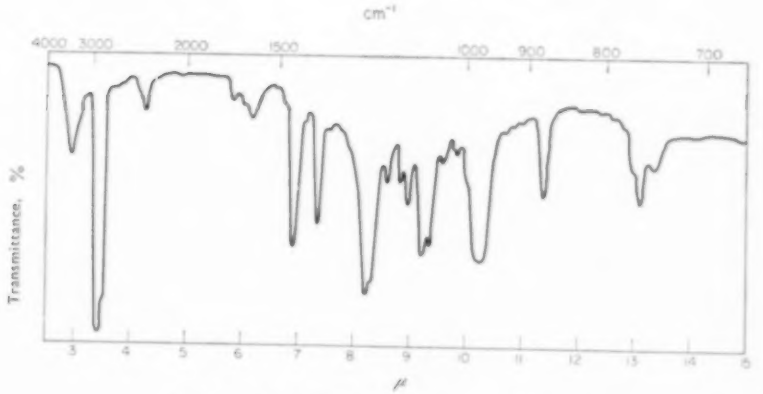

FIG. 2.—Sodium derivative of di-isopropyl phosphite.

RESULTS AND DISCUSSION

The infra-red spectra of a number of di-alkyl phosphites have been recorded[8] and various assignments made. The band at 2435 cm^{-1} was attributed to the P–H stretching vibration. Typical spectra of the salts are shown in Figs. 1–5 and are found to depend markedly on the nature of the metal present. The sodium (Figs. 1 and 2) and magnesium salts are characterized by a P → O absorption at 1220 cm^{-1} a lower frequency than in the free di-alkyl phosphite. The frequency shift in the di-alkyl phosphates upon formation of the sodium salt is to higher frequencies, due to the release from hydrogen bonding.[1] In all the sodium and magnesium salts, the P–H

[8] C. I. MEYRICK and H. W. THOMPSON, *J. Chem. Soc.* 225 (1950).

Vol. 15 1960

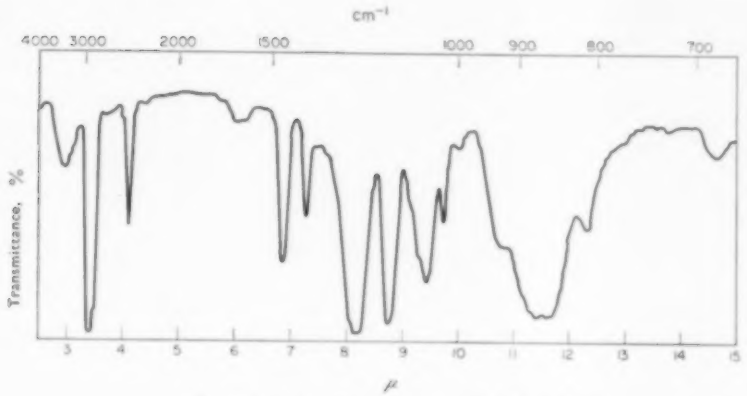

FIG. 3.—Sodium salt of mono-methyl phosphite.

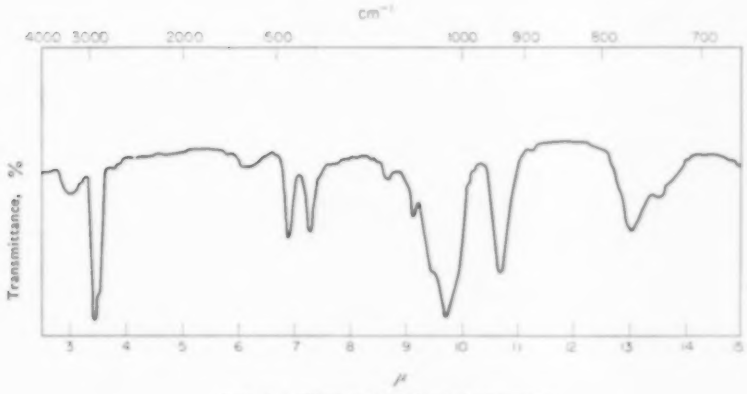

FIG. 4.—Silver salt of di-ethyl phosphite.

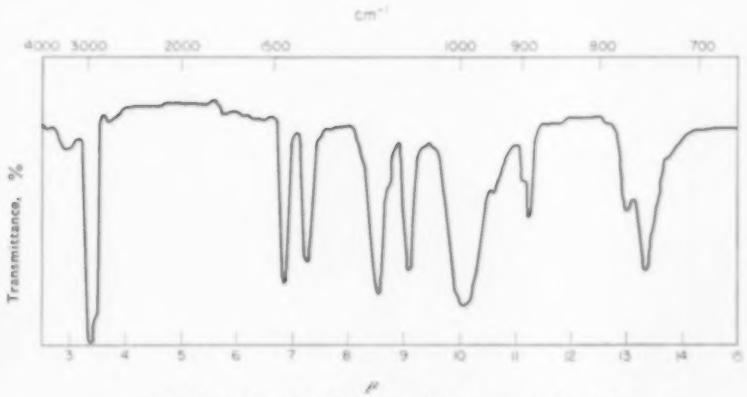

FIG. 5.—Mercuric chloride salt of di-isopropyl phosphite.

absorption disappears, although a much less intense band appears at 2326 cm^{-1}. The reason for this absorption is not clear, and will be referred to in further work. The spectra of the sodium salts of the mono-alkyl phosphites are typified by the spectrum shown for sodium methyl phosphite (Fig. 3) with an intense P–H band at 2439 cm^{-1}, a broad absorption in the 870 cm^{-1} region, and disappearance of the absorption at 1000 cm^{-1}. The broad absorption at 870 cm^{-1} is due to the $P–O^-$ group, and was previously observed in this region in the salts of the di-alkyl phosphates. As in the latter the intensity of this absorption depends on the nature of the ion associated with the $P–O^-$ group, the ferric salts of the mono-alkyl phosphites showing a much reduced absorption in this region.

The silver salts showed a complete absence of absorption due to P–H and P → O group. The spectrum of silver di-ethyl phosphite (Fig. 4) bears a striking resemblance to that of tri-ethyl phosphite,[8] thus substantiating the enol structure assigned by X-ray measurements. A similar argument applies to the mercury salts (Fig. 5) and contrary to previous interpretations it seems to indicate that the mercury derivatives possess the enol structure. From the reactions of the cuprous salts of di-alkyl phosphites it would appear that cuprous ion is similar to silver and mercury in forming an enol derivative. Silver (I), mercury (II) and cuprous ions resemble one another in their combinations with olefines, carboxylic anions, and aminocarboxylic anions, and with alkyl phosphites to yield enol derivatives; this is consistent with the ability of these metal ions to form an oxygen link of considerable covalent character, thus promoting the change to triply-bonded phosphorus. This is also reflected in the behaviour of metal ions towards the di-alkyl phosphate group.[1] The alkali metals show little affinity for the P → O group whilst mercury (II) and silver show considerable interaction; in the case of the di-alkyl phosphites a preliminary weak bonding with the phosphorus would result in a strong interaction with the P → O group and hence a structural change in the anion.

Vol. 15 1960

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PREPARATION OF ORGANOSILICON-SUBSTITUTED BORAZENES*

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(*Received* 27 *October* 1959)

Abstract—The preparation of four B-tris-(triorganosilylmethyl)-N-trimethylborazenes by the Grignard method, of B-tris-(trimethylsiloxy)-N-trimethylborazene using sodium trimethylsilanolate and of B-tris-(triphenylsilyl)-N-trimethylborazene by means of triphenylsilyllithium is described.

The compounds in which the boron and silicon atoms are linked by a methylene group are stable toward hydrolysis, but those containing the B-O-Si and B-Si linkages are not. All are not oxidized by atmospheric oxygen under normal conditions.

OUR recent work[1] concerning the preparation and properties of organosilicon-substituted triorganoboranes has led to interest in organosilicon-substituted boron compounds which might be oxidatively stable. For this reason we have investigated the synthesis and properties of various types of organosilicon-substituted borazenes.

It has been shown recently[2–5] that B-trichloro-N-triorganoborazenes could be alkylated or arylated using the Grignard method. We have used this procedure to prepare several B-tris-(trisorganosilylmethyl)-N-trimethylborazenes (Ia–c), as well as B-tris-(pentamethyldisiloxanylmethyl)-N-trimethylborazene (Id), in good yields. These compounds were stable toward air oxidation and toward hydrolysis under neutral or mildly alkaline conditions. B-tris-(trimethylsilylmethyl)-N-trimethylborazene was not decomposed by alkaline hydrogen peroxide at room temperature. On the other hand, B-tris-(trimethylsiloxy)-N-trimethylborazene (II), prepared by the reaction of sodium trimethylsilanolate with B-trichloro-N-trimethylborazene, was not hydrolytically stable.

The reaction of triphenylsilyllithium with B-trichloro-N-trimethylborazene resulted in the first reported compound containing a boron-silicon bond, B-tris-(triphenylsilyl)-N-trimethylborazene (III).† This crystalline borazene derivative was stable to dry air, but proved to be quite susceptible to hydrolysis, which caused not only Si-B rupture but also complete destruction of the borazene ring

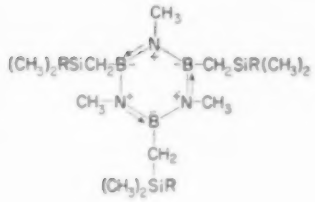
$$[(C_6H_5)_3SiBNCH_3]_3 + 9H_2O \rightarrow 3(C_6H_5)_3SiH + 3B(OH)_3 + 3CH_3NH_2.$$

It was of interest to compare the infra-red spectra of the compounds prepared in

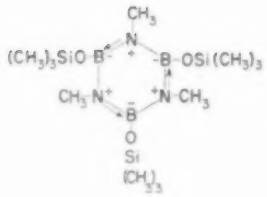
* Presented at the Fifteenth Southwest Regional Meeting of the American Chemical Society, Baton Rouge, December, 1959.

† *Note added in proof*: After our paper was submitted, the communication of COWLEY, SISLER and RYSCHKEWITSCH, *J. Amer. Chem. Soc.* **82**, 501 (1960), appeared in which they described $[(C_6H_5)_2SiBNMe]_3$ as a yellow highly viscous oil. However, their chemical and infra-red data agree with those reported in this paper for our compound of m.p. 248–251°. We can offer no explanation for this difference in physical properties at this time.

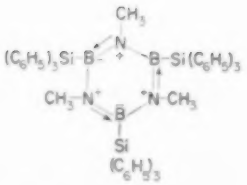
[1] D. SEYFERTH, *J. Amer. Chem. Soc.* **81**, 1844 (1959).
[2] S. J. GROSZOS and S. F. STAFIEJ, *J. Amer. Chem. Soc.* **80**, 1357 (1958).
[3] H. J. BECHER and S. FRICK, *Z. Anorg. Chem.* **295**, 83 (1958).
[4] G. E. RYSCHKEWITSCH, J. J. HARRIS and H. H. SISLER, *J. Amer. Chem. Soc.* **80**, 4515 (1958).
[5] L. F. HOHNSTEDT and D. T. HAWORTH, Abstracts of Papers presented at the 132nd Meeting of the American Chemical Society, New York, September, 1957, p. 8-S.



I a R = CH_3
b R = C_2H_5
c R = n-C_4H_9
d R = $(CH_3)_3SiO$



II



III

this study with those of other B-trisubstituted-N-trimethylborazenes. The effect of the substituents on the boron atom on the B-N bond is apparent from the shift of the intense band assigned by PRICE *et al.*[6] to in-plane vibrations of the borazene ring. Table 1 lists the frequencies given for this band in a number of compounds. The values listed are consistent with the effects on the strength of the B-N bond to be

TABLE 1.—FREQUENCIES DUE TO IN-PLANE VIBRATIONS OF THE BORAZENE RING IN SOME B-TRI-SUBSTITUTED-N-TRIMETHYLBORAZENES

Compound	Borazene ring frequency (cm^{-1})	Ref.
$(CH_3NBCl)_3$	1458	7
$(CH_3NBOCH_3)_3$	1449	7
$(CH_3NBH)_3$	1425	6
$(CH_3NBOC_6H_5)_3$	1412	7
$(CH_3NBOSiMe_3)_3$	1407	this work
$(CH_3NBC_6H_5)_3$	1405	3
$(CH_3NBC_2H_5)_3$	1404	4
$(CH_3NBC_4H_9)_3$	1401	4
$(CH_3NBCH_2CHCH_2)_3$	1401	4
$(CH_3NBCH_2SiMe_3)_3$	1387	this work
$(CH_3NBCH_2SiMe_2OSiMe_3)_3$	1384	this work
$[CH_3NBSi(C_6H_5)_2]_3$	1339	this work

[6] W. C. PRICE, R. D. B. FRASER, T. S. ROBINSON and H. C. LONGUET-HIGGINS, *Disc. Faraday Soc.* **9**, 131 (1950).
[7] M. J. BRADLEY, G. E. RYSCHKEWITSCH and H. H. SISLER, *J. Amer. Chem. Soc.* **81**, 2635 (1959).

Vol. 15 1960

expected for the various substituents on the boron atoms. Thus electron-attracting substituents, such as alkoxy, trimethylsiloxy, phenoxy and phenyl groups, cause a shift to higher frequencies relative to unsubstituted normal alkyl groups, i.e., a strengthening of the B-N bond by withdrawal of electron-density from boron. On the other hand, electron-releasing groups, such as trimethylsilylmethyl and pentamethyldisiloxanylmethyl, cause a shift to lower frequencies, which may be interpreted as a weakening of the B-N bond due to the positive inductive effect of these groups which opposes back donation from nitrogen to boron.

EXPERIMENTAL*

1. *Starting Materials*

The method of BROWN and LAUBENGAYER[8] was used to prepare the quantities of $(MeNBCl)_3$ required. Trimethylchloromethylsilane,[9] ethyldimethylchloromethylsilane,[10] and pentamethylchloromethyldisiloxane[11] are all known compounds and were prepared by established methods. n-Butyldimethylchloromethylsilane, a new compound, was prepared by the reaction of 3·6 moles of $n\text{-}C_4H_9MgBr$ with 3 moles of $Me_2(CH_2Cl)SiCl$ in diethyl ether solution in 34 per cent yield.

$n\text{-}C_4H_9(CH_3)_2SiCH_2Cl$, b.p. 77–78°/29 mm, n_D^{25} 1·4331. (Found: C, 50·31; H, 10·64. Calc. for $C_7H_{17}ClSi$: C, 51·03; H, 10·4%.)

Sodium trimethylsilanolate was prepared by the reaction of sodamide with hexamethyldisiloxane in liquid ammonia solution.[12]

2. B-*tris*-(*Trimethylsilylmethyl*)-N-*Trimethylborazene* (Ia)

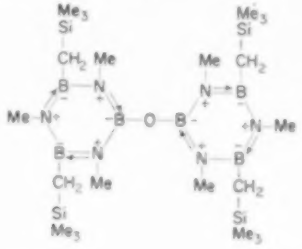
A suspension of 30 g (0·13 mole) of $(MeNBCl)_3$ in 400 ml of anhydrous diethyl ether was prepared in a 2 l. three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel. To this was then added with vigorous stirring during the course of 1 hr the Grignard reagent prepared from 73·5 g (0·6 mole) of Me_3SiCH_2Cl and 14·5 g (0·6 g atom) of magnesium turnings in 350 ml of ether. A white precipitate of $MgCl_2$ formed immediately. The mixture was heated at reflux for 6 hr and left to stand overnight at room temperature. The flask was cooled to 0° and the reaction mixture was hydrolysed with saturated ammonium chloride solution. The organic layer was decanted and the residual salts were washed with three 75 ml portions of ether. The combined organic layer and ether washings were washed with four 100 ml portions of distilled water and subsequently were dried over anhydrous sodium sulphate. Filtration was followed by removal of the ether at reduced pressure. Forty-four grammes of an oily solid remained. To this was added a small quantity of methanol; filtration gave 17 g of white crystalline solid. The filtrate was distilled. The fraction distilling between 110–170° at 0·8 mm crystallized in part in the receiver. The crystals were freed from oil by washing with methanol as before. Further solid was obtained by chilling the methanol washings. In this manner a total of 29 g (58·5 per cent) of compound Ia resulted. An analytically pure sample, m.p. 64°, was obtained by recrystallization from methanol. (Found: C, 47·02; H, 11·29; N, 11·13, B, 8·75; mol. wt. (Rast), 394. Calc. for $C_{15}H_{42}N_3B_3Si_3$: C, 47·25; H, 11·1; N, 11·02; B, 8·51%; mol. wt., 381·3).

During one such preparation a deficiency of Me_3SiCH_2MgCl was inadvertently used, and a small amount of a second substance crystallized from a higher boiling (155–210° at 0·7 mm) fraction on cooling. Recrystallization from methanol gave white crystals, m.p. 95–96°. These were tentatively

* Analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points are uncorrected and were determined on a Fisher–Johns block. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

[8] C. A. BROWN and A. W. LAUBENGAYER, *J. Amer. Chem. Soc.* **77**, 3699 (1955).
[9] F. C. WHITMORE and L. H. SOMMER, *J. Amer. Chem. Soc.* **68**, 483 (1946).
[10] A. D. PETROV, V. F. MIRONOV and N. A. POGONKINA, *Dokl. Akad. Nauk SSSR* **100**, 81 (1955).
[11] R. H. KRIEBLE and J. R. ELLIOTT, *J. Amer. Chem. Soc.* **67**, 1810 (1945).
[12] J. F. HYDE, O. K. JOHANNSON, W. H. DAUDT, R. F. FLEMING, H. B. LAUDENSLAGER and M. P. ROCHE, *J. Amer. Chem. Soc.* **75**, 5616 (1953).

identified as N,N,N,N′,N′,N′-hexamethyl-B,B,B′,B′-tetrakis-(trimethylsilylmethyl)-B,B′-bisborazene oxide. (Found: C, 44·08, 44·32; H, 10·30, 10·29; N, 14·00, 13·97; B, 11·03. Calc. for $C_{22}H_{62}N_6OB_6Si_4$: C, 43·74; H, 10·34; N, 13·91; B, 10·75%.)



Chemical properties of $(MeNBCH_2SiMe_2)_3$

(a) *Thermal stability*. A small sample of compound Ia was placed in a small test tube and the tube was evacuated and sealed off. The tube was then heated at 380° for 30 min. This treatment caused no change in the melting point (64°) of the sample. Heating of the compound in an open test tube at 250° for 15 min caused a lowering of the m.p. to 57–58°. Similarly, distillation of a small sample at atmospheric pressure (bath temperature 250°) lowered the m.p. to 59–60°.

(b) *Hydrolytic stability*. A small sample (213 mg) of the compound was heated at 100° in 20 ml of water for 1 hr. A 98 per cent recovery (209 mg) of the sample was achieved. No change in m.p. was observed after this treatment. No amine odour was noticed when a small sample of compound Ia was refluxed in 2 N NaOH solution for 1 hr. A quantitative recovery of unchanged borazene (m.p. 64°) was obtained. However, no Ia could be recovered after it had been refluxed with 3 N HCl for 1 hr.

(c) *Oxidation stability*. Compound Ia was not affected by alkaline hydrogen peroxide and could be recovered unchanged after being kept at room temperature in this reagent overnight.

It may be noted that SISLER *et al.*[4] found B-trialkyl-N-trimethylborazenes more resistant to hydrolysis and oxidation than borazene itself, reflux with hydrogen peroxide in 50 per cent sulphuric acid being required to effect complete degradation of their compounds.

3. B-*tris*-(*Ethyldimethylsilylmethyl*)-N-*Trimethylborazene* (Ib)

A procedure similar to that described for compound Ia was used in the reaction of the Grignard reagent prepared from 109·4 g (0·8 mole) of $Me_2EtSiCH_2Cl$ and 0·8 g atom of magnesium with 0·15 mole of $(MeNBCl)_3$ in ether solution. Seventy grammes of a light yellow oil resulted which was distilled at reduced pressure. The fraction distilling at 160–185° at 1·0 mm was collected and redistilled to give 38 g (60 per cent) of pure compound Ib b.p. 183–184° at 1·0 mm, n_D^{25} 1·4875, d_4^{24} 0·8977. (Found: C, 51·18; H, 11·31; N, 10·31. Calc. for $C_{15}H_{45}N_3B_3Si_3$: C, 51·05; H, 11·4; N, 9·93%.)

4. B-*tris*-(*n-Butyldimethylsilylmethyl*)-N-*trimethylborazene* (Ic)

A similar procedure was used in the reaction of the Grignard reagent prepared from 132 g (0·8 mole) of $n\text{-}BuMe_2SiCH_2Cl$ and 0·8 g atom of magnesium with 0·17 mole of $(MeNBCl)_3$. After hydrolysis and distillation of the solvent, 110 g of a yellowish oil remained. Distillation at reduced pressure gave 59 g (69 per cent) of crude compound Ic, b.p. 208–217° at 0·8 mm. A second fractional distillation resulted in 43·7 g (57 per cent) of pure material, b.p. 213–214° at 0·9 mm, n_D^{25} 1·4845, d_4^{25} 0·8855. (Found: C, 56·70, 56·96; H, 11·87, 11·93; N, 8·13, 8·17; B, 6·72, 6·60. Calc. for $C_{21}H_{60}N_3B_3Si_3$. C, 56·79; H, 11·92; N, 8·28; B, 6·39%.)

5. B-*tris*-(*Pentamethyldisiloxanylmethyl*)-N-*Trimethylborazene* (Id)

The reaction between 0·8 mole of $Me_3SiOSiMe_2CH_2MgCl$ and 0·15 mole of $(MeNBCl)_3$ in ether solution was carried out using the procedure described above. Distillation of the liquid residue obtained after hydrolysis and distillation of the ether gave 55 g of a fraction distilling at 161–190° at 0·9 mm. A second distillation resulted in 45 g (50 per cent) of colourless compound Id, b.p. 175–176°

at 0·55 mm, n_D^{25} 1·4517, d_4^{25} 0·9158. (Found: C, 41·83%, H, 10·33; N, 7·11; B, 5·88. Calc. for $C_{21}H_{60}O_3N_3B_3Si_3$: C, 41·77; H, 10·02; N, 6·96; B, 5·37%.)

6. B-*tris*-(*Trimethylsiloxy*)-N-*Trimethylborazene* (II)

To a suspension of 37 g (0·165 mole) of $(MeNBCl)_3$ in 300 ml of ether under a nitrogen atmosphere was added during a period of 45 min with vigorous stirring a solution of 88·5 g (0·7 mole) of sodium trimethylsilanolate in 450 ml ether. A slightly exothermic reaction was observed and sodium chloride precipitated. The reaction mixture was refluxed for 6 hr, then was cooled and filtered. Evaporation of most of the ether from the filtrate caused precipitation of some of the excess Me_3SiONa. Filtration was followed by addition of 24 g (0·22 mole) of Me_3SiCl in 150 ml of ether to the filtrate in order to destroy any Me_3SiONa still present by the reaction

$$Me_3SiONa + Me_3SiCl \rightarrow Me_3SiOSiMe_3 + NaCl.$$

Filtration of the precipitated NaCl was followed by distillation of the filtrate. A 60 per cent yield (37·5 g) of compound II, b.p. 129–131° at 0·85 mm, was thus obtained. An analytically pure sample could be gotten by a further fractional distillation (b.p. 130° at 0·85 mm, m.p. 22–23°). (Found: C, 37·37; H, 9·31; N, 11·27; B, 8·22. Calc. for $C_{12}H_{36}O_3N_3B_3Si_3$: C, 37·23; H, 9·37; N, 10·85; B, 8·37%.)

A sample of this compound became turbid on standing in contact with laboratory air. It appeared to be hydrolysed by 2 N NaOH solution.

7. *Preparation of* B-*tris*-(*Triphenylsilyl*)-N-*Trimethylborazene* (III)

A solution of triphenylsilyllithium[13] freshly prepared from 84 g (0·162 mole) of hexaphenyldisilane and 17 g lithium in 400 ml tetrahydrofuran was added with vigorous stirring to a suspension of 21 g (0·093 mole) of B-trichloro-N-trimethylborazene in 500 ml of diethyl ether at such a rate that a gentle reflux was maintained. The brown colour of the $(C_6H_5)_3SiLi$ solution was discharged immediately on addition to the $(MeNBCl)_3$ solution and a white precipitate formed. The mixture was kept at room temperature overnight and then was filtered using a sintered glass filter. The solid was washed with ether and extracted with hot benzene. Evaporation of the benzene left 46 g (55 per cent) of crude product. Recrystallization from benzene and drying *in vacuo* at 70° gave pure B-tris-(triphenylsilyl)-N-trimethylborazene. The substance on heating in a sealed tube under nitrogen appears to shrivel slightly before its melting point of 248–251° is reached.

(Found: C, 75·90; H, 6·23; N, 4·60; B, 3·90; Si, 9·41; mol. wt. (cryoscopic method in benzene), 917. Calc. for $C_{57}H_{54}N_3B_3Si_3$: C, 76·25; H, 6·06; N, 4·68; B, 3·61; Si, 9·39% mol. wt., 898.) In the region where absorptions characteristic of the borazene system are found, the infra-red spectrum of III showed the following bands (in cm^{-1}): 1434 (s), 1425 (sh), 1377 (s), 1359 (s), 1339 (vs). $[(C_6H_5)_3SiBNMe]_3$ is soluble in benzene, chloroform and methylene chloride and poorly soluble in ether and hexane. It decomposes in carbon tetrachloride solution, even in the absence of air. The compound does not appear to be affected by dry air. On being heated in an open test tube it melts to a light yellow liquid which on cooling gives a glassy solid. Heating to higher temperatures (>250°) appears to cause decomposition.

Reactions of B-*tris*-(*triphenylsilyl*)-N-*trimethylborazene*

1. *Hydrolysis.* A solution of 0·3 g of compound III in 30 ml chloroform was shaken with 30 ml of water. The chloroform layer immediately became turbid and methylamine evolution was observed (odour and detection with moist litmus paper). The mixture was shaken for 1 hr and the organic layer was dried over anhydrous calcium chloride. The aqueous phase was alkaline (pH 8–9) and reaction with phenylisothiocyanate indicated the presence of an amine. The infra-red spectrum of the chloroform layer showed a strong band at 2140 cm^{-1} (Si-H) as well as bands at 1435 and 1115 cm^{-1} $[(C_6H_5)_3Si]$ suggesting the presence of triphenylsilane. Weaker absorption in the B-O region was also observed. The remainder of the chloroform solution was evaporated and the residue was extracted with ethanol, leaving a small amount of white powder. The latter was recrystallized twice from hexane and dried *in vacuo* at 40°. This product has not been identified as yet. The ethanol extracts

[13] H. GILMAN and G. D. LICHTENWALTER, *J. Amer. Chem. Soc.* **80**, 608 (1958).

were evaporated at reduced pressure leaving crude triphenylsilane, m.p. 35–41°, identified by comparison of its infra-red spectrum with that of an authentic sample of triphenylsilane.

2. *Bromination.* A solution of 0·3855 g of compound III in 20 ml of chloroform was prepared and titrated with a chloroform solution of bromine (20·64 mg/ml). A permanent yellow colour due to excess of bromine served as a rough indication of the endpoint. The bromine consumption (10·30 ml of the chloroform solution = 6·19 g atom bromine per mole of compound III) suggested that the initial reaction occurring was

$$[(C_6H_5)_2SiBNMe]_3 + 3Br_2 \rightarrow 3(C_6H_5)_2SiBr + (BrBNMe)_2$$

The products of the bromination reaction were examined. During the titration a precipitate had formed. This was filtered and tentatively identified as methylammonium bromide, $[CH_3NH_3]Br$. It was soluble in water, gave a positive test for halide ion with silver nitrate solution and did not contain boron. It melted at 263–264°, and its infra-red spectrum was consistent with this formulation (Found: C, 11·35; H, 5·40; N, 12·49; Br, 70·49. Calc. for CH_6NBr: C, 10·73; H, 5·42; N, 12·50; Br, 71·38%.)

Evaporation of the filtrate in vacuum gave a light-tan, crystalline solid, m.p. 119°, which could be sublimed in vacuum. Two sublimations gave pure triphenylbromosilane, m.p. 120–123° in 56 per cent yield.[14] (Found: C, 64·00; H, 4·58; Si, 8·51; Br, 23·46. Calc. for $C_{18}H_{15}BrSi$: C, 63·71; H, 4·45; Si, 8·28; Br, 23·55%.)

Acknowledgement—This research was supported by the United States Air Force under Contract AF 33(616)-5582, monitored by the Materials Laboratory, Wright Air Development Center, Wright Air Force Base, Ohio.

[14] Melting point reported: 120–121°. P. A. MCCUSKER and E. L. REILLY, *J. Amer. Chem. Soc.* **75**, 1583 (1953).

Vol. 15 1960

Inorg. Nucl. Chem., 1960, Vol. 15, pp. 105 to 109. Pergamon Press Ltd. Printed in Northern Ireland

THE PRODUCTS OF ELECTROLYSIS OF SODIUM AMIDE–POTASSIUM AMIDE EUTECTIC MIXTURE

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(*Received* 23 *September* 1959)

Abstract—The electrolytic products of decomposition of sodium amide–potassium amide eutectic mixture were investigated. The only possibilities of the products at the cathode were sodium metal and potassium metal, hence these were not the main subject of investigation. The anodic products were separated, collected, and identified. The main products identified were ammonia and nitrogen, but positive identification was made of trace amounts of hydrazine. The effect of catalysts present in the molten amides was considered, and potassium amide was prepared without the use of catalytic agents. The electrode material used was graphite of a very high purity, which has no known catalytic effect.

THERE is evidence for the existence of NH_2^- ions in molten sodium amide and potassium amide.[1] Since these fused salts conduct the electric current,[2] it has been suggested that the electrolysis of these salts might produce hydrazine at the anode and the alkali metal at the cathode. When this was attempted, the products were nitrogen and ammonia at the anode and sodium metal at the cathode. This would seem to indicate that if any hydrazine formed it immediately decomposed into nitrogen and ammonia. But since this work was done, a U.S. Patent has been issued for the electrolysis of a formamide solution of calcium amide with the anodic production of hydrazine.[3] Since hydrazine is suseptible to catalytic decomposition, the manner in which the alkali amides were prepared (i.e., the catalytic agent used) could cause, in part, the decomposition of hydrazine into nitrogen and ammonia. To minimize this decomposition, preparation of the alkali amides without the use of catalysts was carried out. For this same reason carbon electrodes were used instead of the usual nickel or platinium. In order to run this at as low a temperature as possible a eutectic mixture of sodium amide and potassium amide was used.

EXPERIMENTAL

Description of apparatus and instruments used

A dry-box, fitted with a glass viewing window and provided with inlets for use of an inert atmosphere, was used for handling the sodium and potassium metals. These had to be "shaved" of their oxide coating, thoroughly dried, weighed, placed in bottles filled with nitrogen and sealed. This presented a fresh surface for the reaction and excluded many of the impurities found in the coatings of these metals.

Carbon electrodes, made from ultra-pure graphite, were obtained from United Carbon Products, Bay City, Michigan.

A direct current source of 0–16 V and 0–10 A was used for the electrical power supply. The electrolytic cell was fabricated from glass tubing and machined Teflon corks secured with brass hold-down bolts.

All the potassium amide used in the experimental work was prepared using the method indicated. Sodium amide was obtained from Farchan Research Laboratories, Cleveland, Ohio. This chemical

[1] C. A. KRAUS, *J. Amer. Chem. Soc.* **30**, 1329 (1908)
[2] L. WOHLER, F. STANG-LUND, *Z. Electrochem.* **24**. 261 (1918).
[3] A. P. STUART (to Sun Oil Co.), U.S. Pat. 2 813 067 (1957).

was analysed for trace impurities of nickel, platinum, palladium and iron, using colorimetric methods. This was considered sufficiently pure to use in the electrolysis.

The preparation of the eutectic mixture was carried out in the dry-box by thoroughly mixing together the proper weights of the two amides. Melting point determinations were used to obtain a mixture with the minimum melting point.

Preparation of potassium amide

A three-necked flask was fitted with a stirrer, reflux condenser, and an addition flask which contained the cut, dried potassium under nitrogen. This flask also had an inlet for the ammonia and was connected to the main flask with a thin rubber tube that acted as a pressure indicator for the addition of the ammonia vapour. The ammonia was started into the flask as soon as the temperature was below −35°C, at which time it began to condense. As soon as the reaction vessel was half filled with liquid ammonia, the metal was added approximately 1g at a time to facilitate solution. As the last of the metal was added, the flask was allowed to warm up to the temperature at which ammonia boils. This temperature was maintained until the amide formed. This usually took 24 hr or longer with continuous stirring. As it went to completion, large amounts of hydrogen gas were evolved, and the amide being insoluble in liquid ammonia, formed a grey slurry which settled to the bottom. The ammonia was allowed to evaporate off over night under a cover of nitrogen. The amide was then transfered to a dry-box where it was scraped out of the flask and stored in nitrogen filled bottles sealed with paraffin wax until ready for use.

Procedure for the electrolysis of the fused salts

The usual procedure for the electrolysis of a fused salt is to run the decomposition just above the melting temperature. With the sodium amide and potassium amide eutectic this would have been at 92°C[4], but one of the possible decomposition products was hydrazine which boils at 113°C (1 atm pressure).[5] Hence the electrolysis was run at 120°C, which permitted the hydrazine to be formed as a vapour and subsequently condensed.

The previously prepared eutectic mixture of the amides was placed in the electrolytic cell under an atmosphere of dry nitrogen as was described for the handling of these salts. This cell, charged with the eutectic mixture was placed in a mineral oil-bath and heated to 120°C by means of an electric hot plate. The graphite electrodes were inserted to the depth of one centimeter in the fused salt. Since the alkali metals produced would be liquid and less dense than the fused salts, the cell was arranged so that the portion containing the anode was slightly elevated, thus preventing the metals from making contact with the anode and shorting out the cell.

Procedure for the determination of the electrolytic products

Since there was the possibility of getting four different products at the anode, a train was set up to trap and separate these substances. The cathode products were not analysed, as the only possibilities were potassium metal and sodium metal.

1. *Determination of hydrazine.* The only product of oxidation that is a liquid at room temperature is hydrazine; hence, the first trap was a U-tube with the bottom immersed in an ice-bath. After each run, the contents of this tube were carefully examined, the tube washed with a minimal amount of water, and the resulting solution submitted to qualitative tests for hydrazine.

2. *Determination of ammonia.* Ammonia, being a vapour at the temperature at which the reaction was carried out, passed through the U-tube in which the hydrazine was trapped and into a standard acid solution with which it reacted. At the end of the electrolytic run the acid solution was titrated with standard base, and by difference the amount of ammonia was determined.

3. *Determination of nitrogen.* After passage through the acid solution which removed all ammonia, and in which the nitrogen was insoluble, the remaining gases were passed through a long tube which contained powdered magnesium. This tube was heated as the gases were passed over it, and the nitrogen reacted with the magnesium forming magnesium nitride. The amount of nitrogen was determined by weight difference before and after reaction. After the first trial in which there was no

[4] C. A. KRAUS and E. J. CUY, *J. Amer. Chem. Soc.* **45**, 712 (1923).
[5] C. D. HODGEMEN (Editor), *Handbook of Chemistry and Physics* (37th Ed.). Chemical Rubber Publishing, Cleveland (1955).

Vol. 15 1960

hydrogen detected, this tube was removed and a calibrated burette was filled with water and the nitrogen was measured by the displacement of water.

4. *Determination of hydrogen.* Upon passing out of the tube of powdered magnesium, the remaining gas was to be collected by displacement of water, and a burette was fitted in a water trough for this purpose. But in the first trial, there was no gas measured by this method; thereafter, this method was used to collect the nitrogen. In each case the gas collected by this method was submitted to the usual qualitative test for hydrogen and was found to be negative each time.

RESULTS AND DISCUSSION

The literature contains several methods for the preparation of the alkali metal amides,[6] but without exception they involve the use of a transition metal or salt of these metals as a catalyst. In the preparation of the potassium amide that was used throughout this work, no such catalyst was used. From the experimental data gathered here, it would seem that the principal role of the catalyst in these reactions was to initiate the formation of the amide, after which the amide itself acts as a catalyst. Our first preparation of potassium amide required 24 hr for completion. During the second preparation a small amount of the previously prepared potassium amide was added to the reaction vessel prior to the addition of the potassium. The fact that the reaction went to completeion within 4 hr, indicated that the amide acted as a catalyst. This method of preparation yields a product whose purity is limited only by the purity of the starting materials and the reacting vessels.

Using the following qualitative tests, it was found that trace amounts of hydrazine were formed, and in each case a positive identification of hydrazine was made. When benzaldelhyde is shaken with a solution of hydrazine, a yellow-orange crystalline material, with a reported melting point of 93°C, separates. An excess of benzaldehyde is to be avoided, as the azine formed is appreciably soluble in the reagent. The compound diethyl aminobenzaldehyde reacts with hydrazine to form an azine which upon addition of a strong acid rearranges to a quinoid structure which possesses an intense orange colour.[7] The melting point of this substance is reported to be 264–266°

MELTING POINTS OF THE HYDRAZINE DERIVATIVES

Run	Benzaldehyde	Dimethylamino-benzaldehyde
I	91–92°C	258–262°C
II	92°C	260–263°C
III	91–92°C	260–264°C

Since a very small amount of any of the catalysts used in the preparation of sodium amide or potassium amide will cause the decomposition of hydrazine, this may explain the small amounts of hydrazine reported in this work, and could also explain why previous workers reported only ammonia and nitrogen as electrolytic decomposition products of the alkali metal amides.

Another important consideration is the matter of the electrode material. The accepted method of electrolysis of conducting materials involves the use of platinum or nickel electrodes. These metals are also used as decomposition catalysts for

[6] W. C. FERNELIUS (Editor), *Inorganic Syntheses* (1st Ed.), Vol. 2, Chap. 38. McGraw-Hill, New York (1946).
[7] L. F. AUDRIETH and B. A. OGG, *The Chemistry of Hydrazine* (1st Ed.). John Wiley, New York (1951).

hydrazine, hence, if they are used as electrodes for the decomposition of the alkali metal amides, any hydrazine so formed could be expected to decompose due to the action of the electrode itself. In this work ultra-pure graphite electrodes were used, which have no known catalytic action on hydrazine. The detection of ammonia was to be expected, in that even under more favourable reaction conditions the disproportionation of hydrazine into ammonia and nitrogen proceeds to a considerable extent.

RESULTS OF THE ELECTROLYSIS

Item	Run I	Run II	Run III
Volts	6·3	8·4	6·5
Current (A)	0·75	1·00	0·78
Time (min)	54·7	60·6	25·6
Faradays ($\times 10^{-2}$)	2·56	3·78	1·24
Moles of eutectic mixture used ($\times 10^{-3}$)	1·75	2·59	0·836
Moles of hydrazine	trace	trace	trace
Moles of ammonia ($\times 10^{-2}$)	2·53	3·77	1·24
Moles of nitrogen ($\times 10^{-2}$)	5·83	8·48	3·77
Moles of hydrogen	None	—	—

The temperature at which the electrolysis was run is also of interest. In the earlier work of the electrolysis of the pure alkali metal amides, the temperatures of the fused salts were necessarily of the order of 200–300°C. Using thermodynamic data available, the following calculations were made regarding the decomposition of hydrazine into

MELTING POINTS OF SODIUM AMIDE–POTASSIUM AMIDE

Compound	Temperature (°C)
$NaNH_2$	220
KNH_2	338
$NaNH_2$–KNH_2 (eutectic)	92

ammonia and nitrogen. This was done for three temperatures: the melting point of the eutectic mixture, the melting point of pure sodium amide, and the melting point of pure potassium amide.[8]

The ΔF° of formation of ammonia is given:[9]

$$\Delta F^\circ = -9500 + 4{\cdot}96T \ln T + 5{\cdot}75 \times 10^{-4}T^2 - 8{\cdot}5 \times 10^{-7}T^3 - 9{\cdot}61T$$

The ΔF° of formation of hydrazine is given:[10]

$$\Delta F^\circ = 27{,}065 - 88{\cdot}922T + 23{\cdot}943T \ln T - 4{\cdot}311 \times 10^{-2}T^2 + 2{\cdot}4244 \times 10^{-5}T^3$$

[8] C. A. KRAUS and E. J. CUY, *J. Amer. Chem. Soc.* **45**, 712 (1923).
[9] E. W. WASHBURN (Editor-in-Chief), *International Critical Tables* Vol. 7, p. 239. McGraw-Hill, New York (1930).
[10] L. F. AUDRIETH and B. A. OGG, *The Chemistry of Hydrazine* (1st Ed.). John Wiley, New York (1951).

Vol. 15 1960

Using the two equations:

$$3N_2H_4 \rightleftharpoons 6H_2 + 3N_2$$
$$2N_2 + 6H_2 \rightleftharpoons 4NH_3$$
$$\overline{3N_2H_4 \rightleftharpoons 4NH_3 + N_2}$$

gives the values for the decomposition of hydrazine. From the ΔF° values thus calculated, and using the relation:

$$-\Delta F^\circ \cong RT \ln K_p$$

the equilibrium constants at the various temperatures were also calculated.

$$\ln K = \frac{-\Delta F^\circ}{RT}$$

At 120°C

$$\log K = \frac{153{,}700}{(2{\cdot}303)(1{\cdot}987)(393{\cdot}2)} = 85{\cdot}44$$

FREE ENERGY CHANGES AND EQUILIBRIUM CONSTANTS

$3N_2H_4 \rightleftharpoons 4NH_3 + N_2$

Temperature (°C)	ΔF° (kcal)	log K
120	−153·7	85·44
220	−170·2	75·42
338	−193·3	69·11

ΔF° is always negative, increasing in negativity with an increase in temperature, but the $\Delta F^\circ/T$ values become less negative with increased temperature and the equilibrium constants thus calculated indicate that less hydrazine will decompose at higher temperatures, assuming the process to be at equilibrium. But from the results of this electrolysis, and that of the previous work, it follows that equilibrium conditions were not approached, and the chemical kinetics of this reaction dictated what the ratio of the final products will be.

There are no data available for the ternary system, potassium amide, sodium amide hydrazine; hence, the possibility of evolved hydrazine dissolving in the liquid eutectic can not be evaluated.

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THE REACTION OF URANIUM OXIDES WITH DINITROGEN PENTOXIDE*

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Abstract—UO_3 reacts with N_2O_5 (liq.) containing N_2O_4 to give a mixture of $UO_2(NO_3)_2 \cdot N_2O_5$ and $UO_2(NO_3)_2 \cdot 2NO_2$. This reaction is erratic; many times only a partial conversion of the oxide is attained. A procedure for preparing NO_2-free N_2O_5 by the oxidation of NO_2 by ozone is described; this procedure is more satisfactory than the dehydration of HNO_3 by P_2O_5. CCl_4 as a solvent for the UO_3–N_2O_5 system apparently yields mixtures of UO_3–$UO_2(NO_3)_2$ and UO_3–$UO_2(NO_3)_2 \cdot N_2O_5$ and/or $UO_2(NO_3)_2$; similarly, 100% HNO_3 as solvent reacts completely with UO_3 to yield mixtures of $UO_2(NO_3)_2 \cdot N_2O_5$ and $UO_2(NO_3)_2 \cdot 2HNO_3$. The mole excess of N_2O_5 used does not affect the product obtained as in the preparation of $Th(NO_3)_4 \cdot 2N_2O_5$. $UO_3(NO_3)_2 \cdot xN_2O_5$, where $x = 0{\cdot}99$–$1{\cdot}09$, may be prepared by the reaction of UO_3 with solid N_2O_5 provided that the particle size of the oxide is small (pass 325 mesh) and the mixture is vigorously stirred. $UO_2(NO_3)_2 \cdot N_2O_5$ may be thermally decomposed to $UO_2(NO_3)_2$ and its thermal stability is less than that of $UO_2(NO_3)_2 \cdot 2NO_2$

Vol. 15 1960

VARIOUS reactions of metal oxides and hydrated nitrates with nitrogen oxides alone, or in nitric acid solutions have been used for the preparation of several anhydrous, nitrates. These methods have been briefly reviewed elsewhere.[1]

In the work reported below we were particularly interested in making a comparison of the reaction of N_2O_5 as against that of N_2O_4 (liq.)[2] on the oxides of uranium. Systems involving the oxides, principally UO_3, have been investigated with liquid N_2O_5 containing N_2O_4, solid pure N_2O_5, and pure N_2O_5 in the solvents water-free CCl_4 and 100% HNO_3.

EXPERIMENTAL

The source and methods of analysis of UO_3 (active), U_3O_8 and NO_2 have been described in a prior paper.[2] The total nitrate content of the products, both "uranyl" -nitrate and N_2O_5 of addition, was determined by a cation exchange resin method similar to that of DAY and co-workers,[3] but substituting Amberlite I.R. 120 resin for Dowex 50.

N_2O_5 was prepared by two methods. In the preliminary studies N_2O_5 was obtained by the dehydration of "white fuming HNO_3" (General Chemical Division Grade, approx. 100% HNO_3) using a modification of the method of GRUENHUT *et al.*[4], in which the acid was added at the bottom of a mixture of glass beads and P_2O_5. The mixture of N_2O_5–N_2O_4 was condensed in a trap on a vacuum line and some of the N_2O_4 pumped off at 10^{-4} mm. Oxygen was then admitted and the condensed mixture melted at 35°. Quantities of liquid N_2O_5–N_2O_4 of the order of 11–13 ml were thus prepared from an excess of P_2O_5 and 45–50 ml of acid. A tapered, 24/40 female joint sealed to the trap held a similar male joint sealed off and to which a calibrated measuring tube was sealed perpendicularly.

* This work was supported in part by the U.S. Atomic Energy Commission under Contract No. AT(11-1)90, Project No. 4, with the Illinois Institute of Technology.

[1] J. R. FERRARO, L. I. KATZIN and G. GIBSON, *J. Amer. Chem. Soc.* **77**, 327 (1955).
[2] G. GIBSON and J. J. KATZ, *J. Amer. Chem. Soc.* **73**, 5436 (1951).
[3] H. O. DAY, JR., J. S. GILL, E. V. JONES and W. L. MARSHALL, *Analyt. Chem.* **26**, 611 (1954).
[4] N. S. GRUENHUT, M. GOLDFRANK, M. L. CUSHING and G. V. CAESAR, *Inorganic Syntheses* Vol. 3, p. 78. McGraw-Hill, New York (1950).

A reaction bulb, also perpendicular to the joint, and at a 30° angle to the measuring tube, contained a measured quantity of the oxide (1·2–2·5 g). A siphon tube ring-sealed through the female tapered joint permitted the transfer of N_2O_5–N_2O_4 by pressure adjustment to the measuring tube. The measured quantity of N_2O_5–N_2O_4 required could be poured into the reaction bulb by rotation of the male joint. At the termination of reaction the excess N_2O_5 and N_2O_4 was pumped out at 10^{-4} mm Hg and 35° for ½–1 hr and the reaction bulb sealed off.

A more satisfactory method from the standpoint of ease of preparation and purity (NO_2-free N_2O_5, was obtained by the oxidation of NO_2–N_2O_4 by ozone.[5] Ozone was produced by a Type. TL, U.S. Ozone Co. of America ozonizer operated at its maximum secondary voltage of 9000 V and an arbitrarily chosen flow meter rate of P_2O_5-dried, tank oxygen of 2 l/min. The ozone was passed through a 20 mm dia. × 150 mm glass tube packed for one-half its length with glass beads. NO_2 introduced through a tube perpendicular to the ozone stream produced sufficient turbulence for complete mixing. The flow rate of NO_2 was so set, with the aid of a flow meter, that the colour of NO_2 was discharged just as the mixed NO_2–O_2 gas stream entered the glass-bead area of the reaction tube. A reasonably constant flow of NO_2 could only be maintained at a room temperature of 30–35°, otherwise the cylinder had to be warmed with a heat lamp. The N_2O_5 collecter, a removable trap, 50 mm dia. × 140 mm and having an exit tube of 15 mm dia. was attached to the reaction tube by means of a ball and socket joint.* The exit tube of the trap led to a P_2O_5 drying tower exhausting into a fume hood. The trap was cooled with a trichloroethylene–CO_2 slush bath. Operating under the above conditions, 6·5 to 7· g of NO_2-free N_2O_5 could be prepared per hour. A running time of over 1 hr generally resulted in the exit tube of the trap being blocked by some of the condensed N_2O_5.

Solutions of 100% HNO_3 plus excess N_2O_5 were prepared in a like fashion after first treating the 100 per cent acid with ozone to convert the small quantity of NO_2 present. The mole ratio of 100% HNO_3 to excess N_2O_5 was determined by titration of a suitably diluted aliquot with 0·1 N NaOH solution. Any necessary transfers were conducted against countercurrents of P_2O_5-dried oxygen or ozone–oxygen to prevent contamination by atmospheric moisture. Manipulation of samples for analysis were carried out in a dry-box.

RESULTS AND DISCUSSION

Oxides in N_2O_5–N_2O_4 (*liq.*). These reactions for the most part were highly erratic. The addition of the first few drops of N_2O_5–N_2O_4 to the oxide produced an active, exothermic reaction, converting some of the oxide to an orange-red material similar in colour to the product observed in the first stages of the thermal decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$. This material was much more resistant to further reaction than the remaining UO_3 and in many instances remained at the end of the overall reaction. We attribute the formation of the orange-red product to a localized thermal decomposition of a rapidly and initially formed $UO_2(NO_3)_2$–N_2O_5 or NO_2 product. Very rapid addition of the N_2O_5–N_2O_4 did not always obviate the difficulty. In those situations where a complete reaction occurred the products were lemon-yellow in colour, completely soluble in water and invariably contained at least a fractional per cent of NO_2. (e.g. Found: U, 47·2; N as NO_3^-, 48·5; NO_2, 5·14; Calc. for: $UO_2(NO_3)_2 \cdot N_2O_5$: U, 47·41; NO_3, 49·40%). These experiments confirmed the existence of a uranyl nitrate–N_2O_5 composition and that relatively small amounts of N_2O_4 present will react more readily with the oxide than N_2O_5. The above observations hold also for U_3O_8 except that, as in the uranium oxide–N_2O_4 reaction,[2] U_3O_8 was more resistant to attack than UO_3. For this reason additional studies were confined exclusively to UO_3 (active). One may consider that N_2O_4 behaves as a solvent in these systems, forming a solvated product containing NO_2. Obviously, if a uranyl

* Other portions of the apparatus were similarly assembled, including the rotameters employed. "Halocarbon" stopcock grease was found most satisfactory as a seal for this work.

[5] D. M. Yost and H. R. Russell, Jr., *Systematic Inorganic Chemistry* p. 18. Prentice-Hall, New York (1944).

nitrate–N_2O_5 were to be prepared N_2O_4 would have to be absent in the N_2O_5 and during the preparative procedure. The ozonization of NO_2 solved the N_2O_5 purity problem and was used for all additional studies reported here. Since N_2O_5 is quite volatile and decomposes readily, time and temperature are important factors which require some compromise in experimental techniques. At the time, a solvent for N_2O_5 appeared to offer a reasonable compromise.

UO_3–N_2O_5 (*as solvent*). Freshly prepared UO_3 and CCl_4 were added to N_2O_5. The head of the trap was then replaced by one having a bubbler tube. Either ozone, or in some experiments, N_2O_5 plus excess ozone was bubbled through the solution containing the UO_3 in suspension for the entire time of the experiment and for 15–30 min after the CCl_4 had been evaporated. A total of twelve experiments were performed with variables as follows: (a) volume of CCl_4 used, 45–110 ml; (b) mole ratios of N_2O_5/UO_3 = 8, 11·5, 13 and 15; (c) evaporation with O_3 vs. O_3–N_2O_5 stream and (d) evaporation at 10, 45 and 50°. Whether or not N_2O_5 was passed through the solution did not seem to be a significant factor. The P_2O_5 exit tube fumed strongly during the initial 10–20 min of the evaporation cycle. Any major reaction probably occurred prior to or during this period. None of the other variables mentioned above appreciably affected the final composition of the product. All samples were uniformly bright orange in colour, quite unlike UO_3 or $UO_2(NO_3)_2$. A major portion of these dissolved readily in water with the minor portion dissolving eventually in 2–5 min to clear yellow solutions, characteristic of the fact that UO_3 dissolves slowly in uranyl nitrate solutions.

As a general summary, these samples may be roughly divided into two classes: (a) those having uranium percentages (e.g. 62·77–63·61) higher than the 60·41 per cent of $UO_2(NO_3)_2$ and low in nitrate (27·39–26·32 vs. 31·47%) and (b) those having approximately equal to or lower uranium percentages (e.g. 54·21–60·04) and higher nitrate (39·05–31·33). In the absence of definitive X-ray data it was believed those samples in category (a) represented $UO_2(NO_3)_2$, but with small percentages of UO_3 and those in (b), of $UO_2(NO_3)_2$ and $UO_2(NO_3)_2{\cdot}N_2O_5$ or possibly $UO_2(NO_3)_2{\cdot}N_2O_5$ plus some unreacted UO_3. A qualitative examination of the experimentally measured arc lengths of X-ray plates of a sample in category (a) indicated some distorted $UO_2(NO_3)_2$ structure and one of (b) a definite $UO_2(NO_2)_3$ structure. Unfortunately, UO_3 (active) did not give a satisfactory pattern permitting its identification in these samples. The solubility behaviour leaves no doubt, however, of the presence of some unconverted UO_3.

UO_3–N_2O_5 (100% HNO_3 *as solvent*). The successful preparation of $Th(NO_3)_4{\cdot}2N_2O_5$[6] suggested a method for $UO_2(NO_3)_2{\cdot}N_2O_5$. The procedure was as described for the CCl_4 solvent system with the exception that excess N_2O_5 and HNO_3 were removed at 10^{-3}–10^{-5} mm pressure. Results obtained are summarized in Table 1. The dry, lemon-yellow, crystalline solids remaining were homogeneous in appearance. This system is markedly different than the corresponding thorium one[5] in that a pure N_2O_5 compound of $UO_2(NO_3)_2$ was not obtained at even the high N_2O_5/UO_3 mole ratio of eleven. Neither the evaporation temperature, the quantity of HNO_3 nor the mole excess of N_2O_5 materially affected the final composition of product; maximum variation was $U \cong 2$, $NO_3^- \cong 0{\cdot}6$ per cent. On the basis of analytical values these products appeared to be mixtures of $UO_2(NO_3)_2{\cdot}N_2O_5$ and $UO_2(NO_3)_2{\cdot}2HNO_3$. Calculated values are respectively, U, 47·41 and 45·77 per cent and total N as NO_3.

[6] J. R. FERRARO, L. I. KATZIN and G. GIBSON, *J. Amer. Chem. Soc.* **77**, 327 (1955).

Vol. 15 1960

49·40 and 47·70 per cent. Insofar as U content is concerned, the values are reasonably compatible; however, the NO_3^- is somewhat too high. The presence of the two solvated aranyl nitrates was confirmed by a quantitative analysis of X-ray data for the two pure, analysed compounds. $UO_2(NO_3)\cdot N_2O_5$ was prepared from UO_3–N_2O_5, solid

TABLE 1.—REACTION OF UO_3 WITH N_2O_5–100% HNO_3 SOLUTIONS

UO_3 (mole)	moles N_2O_5* / mole UO_3 in excess	Vol. (ml) N_2O_5–100% HNO_3	Product analysis	
			U (%)	Total N as NO_3^-(%)
0·0111	0·64	15	46·09	51·42
0·0085	1·10	20	45·76	51·62
0·0103	1·14	25	46·23	51·10
0·0117	2·01	50	44·37	51·71
—	—	—	46·22	51·07†
0·0120	4·75	50	45·79	51·41†
0·0066	8·10	25	45·95	51·22‡
0·0050	11·00	25	45·83	51·24‡

* Represents N_2O_5 in excess less that required to convert the H_2O of reaction, $UO_3 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_2O$, to 100% HNO_3.
† Sample, row 4, heated additional 4 hr at 40–50° at 10^{-5} mm.
‡ Dried at 0–10°; all others, 40–50°.

TABLE 2.—REACTION OF UO_3 WITH N_2O_5(SOLID)

No.	UO_3 (mole)	Pumping time (hr)	Product analysis		Calculated x in $UO_2(NO_3)_2\cdot xN_2O_5$*
			U(%)	Total N as NO_3^-(%)	
1	0·0028	1·25	46·23 ± 0·02	50·29 ± 0·05	1·09
2	0·0035	2·0	46·56 ± 0·00	50·14 ± 0·19	1·06
3	0·0036	2·0	47·31 ± 0·00	48·99 ± 0·09	0·99
4	0·0036	3·0	46·92 ± 0.09	49·76 ± 0·15	1·04
5	0·0036	4·0	46·58 ± 0·03	49·71 ± 0·10	1·05
Calc.: $UO_2(NO_3)_2\cdot N_2O_5$			47·41	49·40	1·00

* Calculated from the average values of columns 4 and 5.

(Sample no. 5, Table 2) and $UO_2(NO_3)_2\cdot 2HNO_3$, by dissolving $UO_2(NO_3)_2$ in 100% HNO_3. The excess acid was removed and the residue dried at 10^{-4} mm and 30°.

UO_3–N_2O_5 (*solid*). Early preliminary experiments with this system, employing N_2O_5 by the dehydration of HNO_3, gave partial reactions and were abandoned in favour of other procedures. Attention was again turned to the solid reaction in a final attempt to prepare pure $UO_2(NO_3)\cdot N_2O_5$. Later experiments proved that lack of

proper mixing and a heterogeneous particle size of the oxide largely accounted for the earlier failures. The final procedure selected included screening the oxide through a 325 mesh screen (in a dry-box) and stirring at high speed with a magnetic stirrer. The oxide and a magnetic stirring bar were placed in the N_2O_5 collecting flask prior to the generation of N_2O_5. After collection of the N_2O_5 and removal of the cooling bath stirring was immediately started. By hand warming the flask-wall and gentle tapping, the sublimed N_2O_5 was caused to drop onto the oxide without melting. A stream of ozone was passed over the solid mixture for the duration of the experiment, including the removal of most of the excess N_2O_5. The remaining excess N_2O_5 was removed on a vacuum line at 10^{-4} mm and 25–30°. Results with a fixed quantity of N_2O_5 (0·091 mole) and screened oxide are given in Table 2.

The solid reaction involved was rather unusual. On stirring the UO_3 and N_2O_5 a light orange mixture is initially produced. In from 5 to10 min, the free flowing powder conglomerated into small beads and gave the appearance of being slightly moist, although no evidence of a liquid appeared and the mass did not stick to or wet the container wall. It was at this point, (temperature of the mixture estimated at between 0–10°), in the span of 0·5 to 1·0 min, that the mixture very rapidly turned bright yellow in colour with no apparent heat of reaction being manifest. In an additional 1–2 min the mixture again became a finely divided, crystalline, free flowing powder. In some of these samples a few bright orange specks were observed (estimated as much less than 0·001 per cent of the total mass) similar in appearance to those found in certain of the liquid N_2O_5–N_2O_4 systems. These again may be due to a minor localized decomposition of the initial product. Examined under low magnification they appeared to have a fused, glassy surface and certainly were not unconverted particles of oxide.

A fractional per cent of N_2O_5 was apparently tenaciously bound in the products to the extent that it could not be removed in a 4 hr pumping time (no. 5, Table 2). no. 3, having the lowest value of x (Table 2), was stored for 14 hr over 1 atm of P_2O_5 dried nitrogen following a 2 hr pumping time. The following day a small quantity of NO_2 was observed in the free space above the sample, which when pumped out, resulted in the NO_2-free 0·99 N_2O_5 composition. These fractional per cents of N_2O_5 over the one mole ratio decompose quite rapidly. All other samples listed in Table 2 were analysed within 3 hr after preparation. Samples nos. 1 and 2 were stored in closed weighing bottles in a desiccator over P_2O_5 for seven and two days, respectively and were then reanalysed (Found U, 47·02 and 46·78; NO_3^-, 48·91 and 49·27%). In both, N_2O_5 had been lost to a composition below $UO_2(NO_3)_2 \cdot N_2O_5$ but the U content, although increasing had not risen correspondingly. $UO_2(NO_3)_2 \cdot N_2O_5$ is extremely hygroscopic and it was believed that these samples had absorbed H_2O even in the comparatively dry atmosphere of a desiccator. Storage for any extended period of time should be done in sealed glass containers.

A portion of no. 5 (0·76 g) was heated to constant weight in 205 min at 10^{-4} mm and 125–130°. A composition corresponding to $UO_3(NO_3)_2$ was obtained. (Found: U, 60·35 ± 0·02; total N as NO_3^-, 31·27 ± 0·35. Calc. U, 60·41; NO_3^-, 31·47%). The above observations indicated that $UO_2(NO_3)_2 \cdot N_2O_5$ has a lower thermal stability and is more hygroscopic than $UO_2(NO_3)_2 \cdot 2NO_2$.

Vol. 15 1960

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COMPLEXITY OF TITANIUM(IV) FLUORIDE SOLUTIONS

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Abstract—The complexity of solutions of titanium(IV) and fluoride ions has been investigated in a constant ionic medium (3 M ClO_4^-) at 25° by means of potentiometric titrations with a quinhydrone electrode. The complex formation is entirely mononuclear and the highest complex is found to be $TiOF_4^{2-}$. All equilibrium constants have been calculated with the exception of $TiOF^+$, the the formation constant of which cannot be found by hydrogen ion measurements. The following equilibrium constants were found:

$$TiOF^+ + F^- \rightleftarrows TiOF_2 \qquad \log \beta_1 = 4{,}35\ M^{-1}$$
$$TiOF^+ + 2F^- \rightleftarrows TiOF_3^- \qquad \log \beta_2 = 8{,}31\ M^{-2}$$
$$TiOF^+ + 3F^- \rightleftarrows TiOF_4^{--} \qquad \log \beta_3 = 12{,}03\ M^{-3}$$

THOUGH it is well known that titanium(IV) is strongly complexed by fluoride no quantitative evaluation has been made of the complexes which are formed in aqueous solutions. Various investigators report[1] that a dihydrate $TiF_4 \cdot 2H_2O$ may be crystallized from a solution of titanium oxide in hydrofluoric acid and that this compound in solution slowly hydrolyses, yielding an oxyfluoride $TiOF_2$. Fluotitanates are also described as salts derived from the hypothetical H_2TiF_6, which is said to be a strong acid. The existence of TiF_6^{2-} was suggested as long ago as 1908.

Recently WOODS and COCKERELL[2], from studies of the absorption on strongly basic ion-exchange resins, claim that titanium(IV) is adsorbed as TiF_5^- or a higher complex. The only quantitative result available is given by KLEINER[3], who by means of spectrophotometric measurements calculated the formation constant for $TiOF^+$ as $\log \beta_1 = 6{\cdot}44$.

In the studies of titanium(IV) solutions there is considerable uncertainty regarding the ionic species which may be present, and whether titanium(IV) exists as Ti^{4+} or TiO^{2+}. In a potentiometric investigation of titanium(IV) hydrolysis[4] it has been shown that the Ti^{4+} ion does not exist at all in aqueous solutions. Up to a very high acid concentration ($[H^+] = 0{\cdot}4$ M) the ion TiO^{2+} is the only species of titanium present. The effect of higher acidities upon the nature of this species was investigated in the present work by comparing the optical absorbancy of a titanium(IV) solution over a range of hydrogen ion concentrations up to 5 M $HClO_4$ (Fig. 1). It was found that the plot of optical density (D/M) against the wavelength was independent of titanium concentration in the range $10 \leq M \leq 73$ mM and of $[H^+]$ in the range $5 \leq [H^+] \leq 0{\cdot}2$ M. Therefore we may conclude that the titanyl ion may be regarded as a stable entity which behaves similarly to a metal ion having a constant charge within wide limits of acidity.

[1] J. H. SIMONS, *Fluorine Chemistry*. Academic Press, New York (1950).
[2] P. H. WOODS and L. COCKERELL, *J. Amer. Chem. Soc.* **80**, 1534 (1958).
[3] K. E. KLEINER, *Zh. Obshch. Khim.* **22**, 17 (1952).
[4] L. CIAVATTA. Unpublished results (1959).

When the pH of an acid solution of titanyl perchlorate is increased, hydrolysis occurs, and even at high values of $[H^+]$ (200 mM), this reaction is noticeable. Studies on complexes formed by TiO^{2+} are quite difficult because these equilibria are always complicated by hydrolysis unless the complex is a very strong one.

The complex-formation between TiO^{2+} and fluoride has been studied by potentiometric titration, the complexity of hydrogen fluoride solutions being determined in a

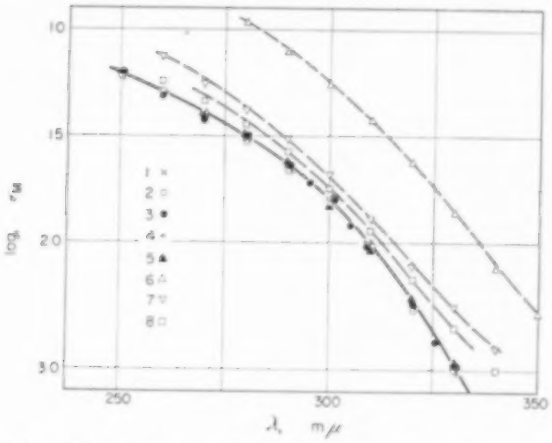

FIG. 1.—Absorption spectra of titanyl ion in acid solution (ClO_4^- = 3 M). Full line: non-hydrolysed solutions. Broken lines: hydrolysed solutions.

(1) C_M = 10·0 mM H = 207·6 mM
(2) C_M = 20·0 mM H = 455·1 mM
(3) C_M = 72·9 mM H = 1514 mM
(4) C_M = 35·0 mM H = 811·6 mM
(5) C_M = 36·5 mM H = 5 M
(6) C_M = 170·5 mM H = 105·8 mM
(7) C_M = 19·1 mM H = 170·0 mM
(8) C_M = 20·0 mM H = 206·6 mM

previous investigation.[5] The reaction of a metal ion with a ligand when hydrolysis occurs can be represented, omitting charges for clarity, by the following expression:

$$pM + qH_2O + nA \rightleftarrows M_p(OH)_qA_n + qH^+ \qquad (1)$$

where p, q and n are integral. If the ionic strength of the solution is large and constant, activity factors can be considered constant and the stoicheiometric formation constant can be written:

$$K_{p,q,n} = \frac{[M_p(OH)_qA_n][H^+]^q}{[M]^p[A]^n} \qquad (2)$$

The formation function $\bar{n}$ is dependent therefore on [A], [M] and $[H^+]$:

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{\Sigma_p\Sigma_q\Sigma_n nK_{p,q,n}[M]^p[H^+]^{-q}[A]^n}{[M] + \Sigma_p\Sigma_q\Sigma_n p[M]^p[H^+]^{-q}[A]^n} \qquad (3)$$

p, q and n can take values from 1 to P, 0 to Q and 1 to N, respectively.

If the formation function is found to be independent of $[H^+]$ no hydrolytic equilibria occur in solution. If $\bar{n}$ is independent of [M], polynuclear reactions can be ignored and only mononuclear complexes should exist in solution.

[5] L. CIAVATTA and A. LIBERTI. Unpublished results (1959).

Vol. 15 1960

In the absence of hydrolytic and polynuclear reactions equation (3) is therefore simplified to:

$$\bar{n} = \frac{\sum_1^N n\beta_n[A]^n}{1 + \sum_1^N \beta_n[A]^n} \tag{3a}$$

where $\beta_n = K_{1,0,n}$

The existence of polynuclear complexes may be checked by working at different values of C_M, and the contribution of non-hydrolytic complexes may be found by making measurements in more acid solutions and extrapolating to $[H^+]^{-q} \to 0$.

Calculation of $\bar{n}$ and [A] *by e.m.f. measurements*

Since no reversible electrodes are available to measure the free concentrations of fluoride and of titanyl ions, only $[H^+]$ can be determined by experiment.

In the absence of fluoride ions and of hydrolysis $[H^+] = H$, where H is the analytical concentration of hydrogen ion. When sodium fluoride is added to an acid solution of titanyl perchlorate, in addition to reaction (1) F^- is also bound to H to form HF and HF_2^-.

For the material balance we can write, neglecting hydrolytic equilibria and assuming that only F^- behaves as a ligand:

$$H = [H^+] + K_{11}[H^+][A] + K_{12}[H^+][A]^2 \tag{4}$$

The formation constants of the proton–fluoride system in 3 M $NaClO_4$ are: $\log K_{11} = 3{\cdot}27\ M^{-1}$ and $\log K_{12} = 4{\cdot}36\ M^{-2}$

By rearranging equation (4):

$$H/[H^+] = 1 + k_{11}[A] + K_{12}[A]^2 \tag{5}$$

Since $[H^+]$ is measured and H is known from the composition of the solutions equation (5) can be solved for [A].

The formation function is calculated from the expression

$$\bar{n} = \frac{C_A - [A] - Z \cdot H}{C_M} \tag{6}$$

where C_A and C_M are respectively the total analytical concentrations of fluoride and titanium, and Z is the average number of complex-bound fluoride ions per hydrogen atom. When $[H^+]$ and [A] are known, it can be calculated by means of the expression

$$ZH = K_{11}[H^+][A] + 2K_{12}[H^+][A]^2 \tag{7}$$

The relationship (7) holds when hydrolytic equilibria can be neglected; should this occur, equation (7) can be obtained by extrapolation to $C_M \to 0$.

EXPERIMENTAL

Apparatus

The titration cell was of the type described by FORSLING *et al.*[6] The reference electrode was:

$$Ag/[Ag^+] = 10\ mM, [Na^+] = 2990\ mM, [ClO_4^-] = 3000\ mM/NaClO_4 = 3000\ mM// = RE$$

The silver electrode was prepared as recommended by BROWN[7]. Measurements of the free hydrogen ion concentration were made with a quinhydrone electrode:

$$RE\ //\ [H^+], [ClO_4^-] = 3000\ mM/QH_2—Q—/Pt$$

[6] W. FORSLING, S. HIETANEN and L. G. SILLÉN, *Acta Chem. Scand.* **6**, 901 (1952).
[7] A. S. BROWN, *J. Amer. Chem. Soc.* **56**, 646 (1934).

Quinhydrone electrodes were bright platinum foils which were cleaned before use with 50% HNO_3 washed with water and ignited in an alcohol flame.

An extinctiometric investigation was carried out in order to check whether a reaction occurs between titanyl ion and quinhydrone. It was found that slight complex formation takes place; it seems however that this interaction may be neglected, since no variation of the quinhydrone spectrum was observed when the ratio fluoride/titanyl ion was about one. According to the conclusions of this research this behaviour does not affect the experimental results.

Attempts were made to measure the free hydrogen ion concentration of titanyl solutions by means of a hydrogen electrode, but reproducible potential values were not obtained. Since detectable amounts of chloride ions were found in the solution it seems very likely that titanium(IV) is reduced to titanium(III) which is responsible for the reduction of perchlorate.

e.m.f. measurements were performed to 0·01 mV with an SEB potentiometer (Milano). In all cases the potentials were stable within 0·1 mV.

All parts of the apparatus which were in contact with the solutions were constructed in polystyrene.

Chemicals

Titanyl perchlorate solutions were prepared as follows: titanyl sulphate $TiOSO_4$, $2H_2O$, prepared as recommended by PAMFILOV *et al.*[8], was treated in a beaker with Montecatini C-300 cation exchange resin in hydrogen form until exchange was complete. The resin was washed free from SO_4^{2-} with water; then a glass column (32 cm length, 3·5 cm diameter) was filled with the resin and exchange carried out with 1·5 M perchloric acid. The eluate was tested for SO_4^{2-} and Fe^{3+}; these ions were absent. The titanium content of the solution was determined by igniting a known volume of the solution at 800°C in a platinum crucible. The perchlorate concentration was determined by flowing a sample of solution through a cation resin in hydrogen form and titrating the eluate with NaOH. Thus the free hydrogen ion concentration was known:

$$[H^+] = [ClO_4^-] - 2[TiO^{2+}]$$

Sodium fluoride solutions were prepared from analytical grade Merck's product without further purification. The concentration of the stock solutions was checked by ion exchange and subsequent acidimetric titration. The results agreed within 0·2 per cent.

Perchloric acid was of analytical grade; the concentration of stock solutions was determined by titration with Na_2CO_3 using methyl-red and bromo-cresol green as visual indicators.

Sodium perchlorate was prepared by neutralizing $HClO_4$ with sodium hydrogen carbonate to the extent of 98 per cent and boiling off CO_2. Neutralization was complete with NaOH. The solution was filtered to remove the iron and silicon which were precipitated. The salt concentration was determined by evaporating a known amount of solution in an electric oven at 125°C; the sample was dried and weighed as $NaClO_4$.

Sodium hydroxide solutions were prepared from 50% NaOH and stored in plastic bottles. Stock solutions were standardized with $HClO_4$ and by evaporation of a known amount after addition of hydrochloric acid in slight excess. The sample was dried at 360°C and weighed as NaCl. The results agreed within 0·1 per cent.

Silver perchlorate solutions were prepared by boiling diluted $HClO_4$ with excess of Ag_2O. The solutions were standardized by Volhard's method.

Quinhydrone (Merck) was free of iron and alkali, and was used without purification.

Procedure

This study has been carried out by means of potentiometric titrations at 25°C in a thermostat. In order to use concentrations instead of activities in the formulae for e.m.f. and for equilibrium constants, all solutions were made 3 M in ClO_4^- by the addition of sodium perchlorate. Solutions were mixed by a stream of nitrogen, purified by passing over copper at 400°C, and then through 10% H_2SO_4, 10% NaOH, and 3 M $NaClO_4$ solutions, the last in order to equilibrate the gas at the correct aqueous vapour pressure.

An acid–base determination was first made to calculate the value of E_0. The measured e.m.f. E is related to H by:

$$E = E_0 + E_j + 59{\cdot}16 \log [H^+] \qquad (8)$$

[8] A. V. PAMFILOV and T. A. KUDIATOVA, *Chem. Abstr.* **44**, 1354 (1950).

Vol. 15 1960

where, in the absence of the complexing agents, $[H^+] = H$, the total analytical concentration, E_0 is a constant and E_j is the liquid junction potential, which is approximately given by $E_j = -j[H^+]$. By plotting the experimental values $E - 59{\cdot}16 \log [H^+] (= E_0 + j[H^+])$ against $[H^+]$ a straight line is obtained; by extrapolating to $[H^+] \to 0$, E_0 is found. The slope of the straight line gives j, which is a constant around $0{\cdot}017 \pm 0{\cdot}001$ mV mM.

Known amounts of sodium fluoride were added to the cell from a calibrated burette together with a solution of titanyl perchlorate. The total analytical concentration of TiO^{2+} was kept constant during the titration; this is not essential but greatly simplifies the calculations.

TABLE 1.—DETERMINATION OF CORRESPONDING VALUES OF $\bar{n}$ AND [A] FROM POTENTIOMETRIC MEASUREMENTS OF $[H]^+$ WITH QUINHYDRONE ELECTRODE

$C_M = 15{\cdot}07$ mM $H = 189{\cdot}2$ mM

A (mM)	H (mM)	C_M (mM)	$[H^+]$ (mM)	$H/[H^+]$	ZH (mM)	$\bar{n}$	log [A] (mM)
19·93	189·2	15·07	188·0	1·0065	1·42	1·23	−2·398
26·02	185·1	14·74	180·4	1·0261	4·73	1·44	−1·854
31·85	181·2	14·43	171·9	1·0539	9·61	1·54	−1·523
37·33	177·5	14·13	164·7	1·0772	12·62	1·74	−1·387
42·64	173·9	13·84	157·1	1·1071	16·98	1·86	−1·237
47·84	170·4	13·56	150·1	1·1348	19·50	2·10	−1·150
52·74	167·1	13·30	143·0	1·1677	22·60	2·26	−1·070
57·45	163·9	13·05	137·3	1·1933	24·60	2·50	−1·001
62·03	160·8	12·80	130·6	1·2306	29·02	2·67	−0·920
66·36	158·2	12·57	125·5	1·2603	31·60	2·75	−0·854
70·61	155·0	12·34	120·0	1·2912	34·96	2·88	−0·807
74·63	152·3	12·12	114·9	1·3255	37·52	3·05	−0·760
78·55	149·6	12·02	109·4	1·3676	40·28	3·20	−0·708
82·38	147·0	11·71	102·9	1·4291	44·45	3·23	−0·639
86·04	144·6	11·50	97·2	1·4872	47·52	3·32	−0·585
89·64	142·1	11·20	91·2	1·5580	51·11	3·39	−0·528
96·38	137·6	10·95	79·5	1·7309	58·56	3·43	−0·409

When E_0 and j are known and E is measured, H can be obtained from equation (8). From the composition of the solution the total concentrations of metal and of ligand (C_M and C_A respectively) are known and by means of (5), (6) and (7) the values for [A], n and ZH are calculated.

RESULTS

The first addition of sodium fluoride to a titanyl perchlorate solution which is not hydrolysed causes no detectable change in hydrogen ion concentration; this indicates that the fluoride ion is very strongly bound and therefore the first step formation constant cannot be evaluated by direct potentiometric measurements of hydrogen ion concentration.

A measurable decrease in hydrogen ion concentration is observed in hydrolysed solutions. Since for these solutions the ratio $H/[H^+] \leq 1$ these variations should obviously be attributed to repression of the hydrolysis of the metal ion by fluoride complex formation. When the ratio C_A/C_M becomes higher than one, A is bound also to H^+ and from the variations in the ratio $H/[H^+]$ the equilibria due to the other complexes may be calculated.

Table 1 gives an example of the potentiometric titration carried out at $C_M = 15{\cdot}07$

Table 2.—The formation function $\bar{n}$ at corresponding values of [A] for different total concentrations of C_M, by potentiometric measurements

$C_M = 10{\cdot}0$ mM $H = 100{\cdot}0$ mM		$C_M = 15{\cdot}0$ mM $H = 150{\cdot}0$ mM		$C_M = 10{\cdot}29$ mM $H = 165{\cdot}4$ mM		$C_M = 5{\cdot}00$ mM $H = 50{\cdot}0$ mM	
$\bar{n}$	log [A]	$\bar{n}$	log [A]	$\bar{n}$	log [A]	$\bar{n}$	log [A]
1·39	−2·125	1·42	−1·960	1·21	−2·194	1·45	1·820
1·54	−1·660	1·93	−1·290	1·38	−1·793	1·69	−1·390
1·68	−1·456	2·18	−1·170	1·56	−1·585	2·00	−1·315
1·85	−1·334	2·36	−1·080	1·78	−1·398	2·34	−1·080
2·04	−1·250	2·47	−1·020	1·90	−1·284	2·57	−0·980
2·33	−1·122	2·62	0·955	2·09	1·194	2·95	−0·715
2·59	−1·040	2·69	−0·900	2·25	−1·135		
2·76	−0·885	2·80	−0·860	2·46	−1·071		
2·83	−0·824	2·88	−0·820	2·50	−0·996		
2·93	−0·780	2·84	−0·745	2·63	0·929		
3·03	−0·660	2·87	−0·730	2·78	−0·876		
3·18	−0·630	2·89	−0·700	2·82	−0·810		
				3·05	−0·693		
				3·14	−0·635		
				3·28	−0·579		

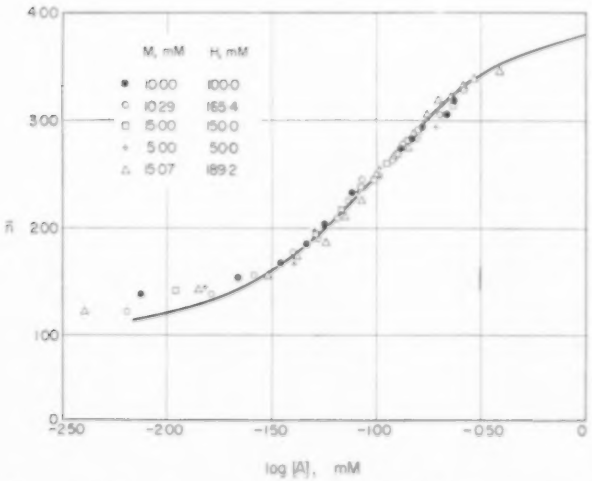

Fig. 2.—The complex formation curve at different values of C_M and H. Full curve calculated from the complexity constants obtained from the potentiometric measurements.

mM and $H = 189{\cdot}2$ mM. The results of the main titration are collected in Table 2 and plotted in Fig. 2.

The formation curve starts at $\bar{n} = 1{\cdot}00$ and reaches a maximum at $\bar{n} = 4{\cdot}00$; therefore the highest complex present in solution is $TiOF_4^{2-}$. Since the experimental points for different metal and hydrogen ion concentrations fall on the same curve polynuclear and hydrolytic equilibria can be ignored.

Vol. 15 1960

From a plot of $\bar{n}$ as a function of log [A] the formation constants for the following equilibria may be calculated:

$$TiOF^+ + F^- \rightleftharpoons TiOF_2$$

$$TiOF^+ + 2F^- \rightleftharpoons TiOF_3^-$$

$$TiOF^+ + 3F^- \rightleftharpoons TiOF_4^-$$

This calculation has been carried out by two methods.

(*a*) *Bjerrum's spreading factor method*[9]

The slope of the formation function $\bar{n}$ vs. log [A] at its midpoint is obtained from Fig. 2 where $N = 3$

$$\Delta = \left(\frac{d\bar{n}}{d \log [A]}\right)_{n=N/2} \cdot 0{\cdot}434 = 0{\cdot}952 \tag{8}$$

From this value of Δ, the spreading factor was calculated by means of the expression

$$x^2 = \frac{9 - 4\Delta}{12\Delta - 3} \tag{9}$$

which on solution gives $x = 0{\cdot}785$.
By means of the relationship:

$$\log k_n = \log K + \log \frac{N + 1 - n}{n} x^{N+1-2n} \tag{10}$$

where $\log K = -\log[A]_{\bar{n}=N/2} = 4{\cdot}00$

the following provisional formation constants were calculated:

$$\log k_{11} = 4{\cdot}26\ M^{-1} \qquad \log \beta_1 = 4{\cdot}26\ M^{-1}$$
$$\log k_2 = 4{\cdot}00\ M^{-1} \qquad \log \beta_2 = 8{\cdot}26\ M^{-2}$$
$$\log k_3 = 3{\cdot}73\ M^{-1} \qquad \log \beta_3 = 11{\cdot}99\ M^{-3}$$

(*b*) *Fronaeus' method*[10]

The formation function $\bar{n}$ as a function of log [A] may be written in the form:—

$$\frac{\bar{n} - 1}{[A]} = \frac{d \ln X([A])}{d[A]} \tag{11}$$

where

$$X([A]) = 1 + \sum_1^N \beta_n [A]^n$$

From the experimental data shown in Fig. 3, by graphical integration, FRONAEUS' function $X([A])$ was calculated:

$$X([A]) = \exp \int_0^{[A]} \frac{\bar{n} - 1}{[A]} d[A] = \sum_0^N \beta_n [A]^n$$

The complexity constants can be calculated by introducing a new function $X_1([A])$:

$$X_1([A]) = \frac{X([A]) - 1}{[A]} = \beta_1 + \beta_2[A] + \beta_3[A]^2 \tag{13}$$

[9] J. BJERRUM, *Metal Ammine Formation in Aqueous Solutions*. P. Haase, Copenhagen (1957).
[10] see S. AHRLAND, *Acta Chem. Scand.* **3**, 783 (1949).

The plot of X_1 ([A]) against [A] gives a curve which is easily extrapolated to [A] = 0; the intercept on the axis gives β_1 and the slope at the intercept is equal to β_2. The latter constant is more accurately determined by calculating a new function X_2 ([A]):

$$X_2([A]) = \frac{X_1([A]) - \beta_1}{[A]} = \beta_2 + \beta_3[A]$$

which by extrapolation allows β_2 to be calculated as the intercept on the axis and β_3 as the slope at the intersection. The function X_3 ([A]) is practically constant over the

TABLE 3.—X_1([A]), X_2([A]) AND X_3 ([A]) AS FUNCTIONS OF [A]

[A]	ln $X([A])/X([A_0])$	$X([A])/X([A_0])$	$X([A])$	$X_1([A])$	$X_2([A])$	$X_3([A])$
0·01	—					
0·02	0·2337	1·26	1·58	29·0		
0·03	0·4517	1·57	1·96	32·0		
0·04	0·6550	1·92	2·40	35·0		
0·05	0·8463	2·32	2·90	38·0	310	
0·06	1·0263	2·78	3·47	41·2	312	
0·07	1·1963	3·30	4·13	44·6	315	
0·08	1·3587	3·86	4·84	48·0	318	
0·09	1·5015	4·45	5·55	50·5	312	
0·10	1·6637	5·25	6·58	55·8	333	
0·12	1·9437	6·92	8·65	64·0	346	
0·14	2·2037	9·08	11·40	74·2	370	
0·16	2·4463	11·35	14·20	82·5	375	1065
0·18	2·6737	14·4	18·00	94·0	396	1065
0·20	2·8887	17·8	22·20	105·0	412	1040
0·22	3·0913	21·8	27·40	120	445	1090
0·24	3·2813	26·3	32·80	132	456	1050
0.26	3·4613	31·6	39·40	147·5	481	1065
0·28	3·6315	37·3	46·40	163	503	1070
0·30	3·7937	43·9	54·90	179	522	1060
0·34	4·0987	59·2	74·00	215	566	1065
0·38	4·3737	79·3	99·00	258	618	1060

whole [A]-range so that X_3 ([A]) = β_3. In Table 3 the values of X_1([A]), X_2([A]) and X_3([A]) obtained from the data of Fig. 3 have been calculated. In Fig. 4 the functions X_1 ([A]) and X_2 ([A]) are plotted and from the graph the following values of the formation constants have been obtained:

$$\beta_1 = 2{\cdot}25 \times 10^4\ M^{-1} \qquad \log \beta_1 = 4{\cdot}35\ M^{-1}$$
$$\beta_2 = 2{\cdot}04 \times 10^8\ M^{-2} \qquad \log \beta_2 = 8{\cdot}31\ M^{-2}$$
$$\beta_3 = 1{\cdot}06 \times 10^{12}\ M^{-3} \qquad \log \beta_3 = 12{\cdot}03\ M^{-3}$$

The agreement between the methods is fairly good and the latter values of the constants can be considered definitive. In Fig. 5 is shown the distribution of the four complexes $TiOF^+$, $TiOF_2$, $TiOF_3^-$ and $TiOF_4^{2-}$ as a function of [A].

DISCUSSION

The potentiometric investigation of the fluoride–titanyl system shows that in the metal concentration range $5{\cdot}0 < C_M < 15{\cdot}0$ mM and the hydrogen ion range 200

Vol. 15 1960

$< [H^+] < 50$ mM a series of mononuclear complexes is formed, viz. $TiOF^+$, $TiOF_2$, $TiOF_3^-$ and $TiOF_4^{2-}$. Though the hydrogen ion concentration has been kept high in order to repress hydrolysis of titanyl ion and to permit detectable variations of $[H^+]$ even at low values of fluoride concentration, the formation constant of $TiOF^+$

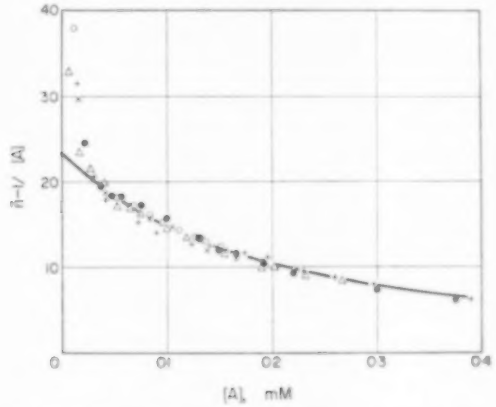

FIG. 3.—$\bar{n} - 1/[A]$ as a function of [A], the integration of which gives the $X([A])$ function.

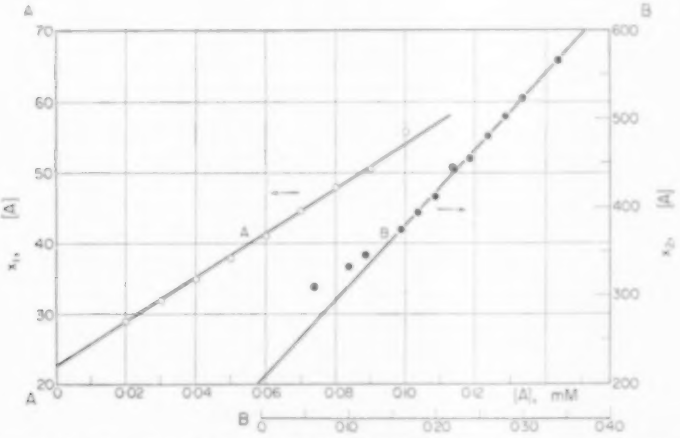

FIG. 4.—The functions $X_1([A])$(line A) and $X_2([A])$(line B) which give the complexity constants.

cannot be calculated from experimental data obtained by potentiometric titrations. An estimate of its value may be obtained by taking into consideration the sensitivity of the experimental techniques which have been employed.

If the minimum detectable variation of E, ΔE, is 0·2 mV, the corresponding variation of $\Delta[H^+]$ will be, according to (8):

$$\Delta E = j\,\Delta[H^+] + 59{\cdot}16\,\frac{\Delta[H^+]}{[H^+]}\,0{\cdot}434 \cong 59{\cdot}16\,\frac{\Delta[H^+]}{[H^+]}\,0{\cdot}434 \qquad (15)$$

But from equation (5) it follows that

$$\frac{H - [H^+]}{[H^+]} = \frac{\Delta[H^+]}{[H^+]} = k_{11}[A] + k_{12}[A]^2 \qquad (16)$$

By taking $\Delta E = 0{\cdot}2$ mV and H = 200 mM, then from (15) and (16), $[A] = 4{\cdot}2 \times 10^{-6}$ Thus the formation constant of the first complex should be higher than $1/[A] = 2{\cdot}4 \times 10^5$.

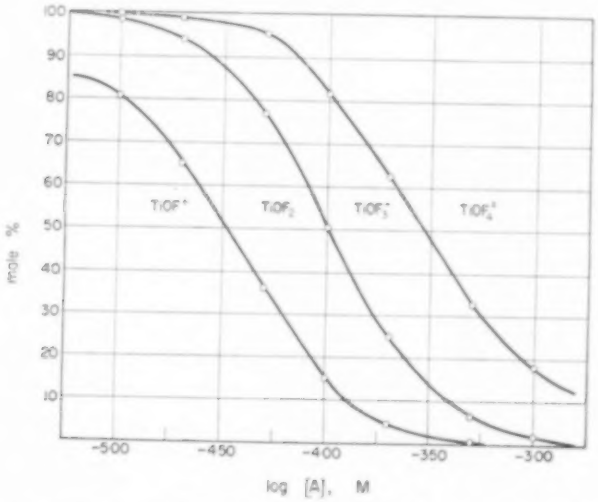

FIG. 5.—Distribution of complexes of titanyl and fluoride as a function of the logarithm of fluoride concentration, using the constants calculated in this work.

As far as the hexafluotitanate ion is concerned its existence in the range of hydrogen ion concentration which has been investigated must be ruled out, since $\bar{n}$ tends to four and the highest complex formed is therefore $TiOF_4^{2-}$. The non-existence of TiF_6^{2-} in acid solution is in agreement with the results obtained in work on the hydrolysis of fluotitanates,[11] where it was found that the hydrolysis takes place in two steps: a very fast reaction consuming two equivalents of alkali and a fairly slow reaction. In the light of these results it seems that TiF_6^{2-} hydrolyses almost instantaneously to $TiOF_4^{2-}$, which slowly undergoes further hydrolysis.

[11] A. LIBERTI and L. CIAVATTA, *J. Inorg. Nucl. Chem.* **8**, 365 (1958).

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COMPOSITION AND STABILITY OF SOME METAL–5-SULPHOSALICYLATE COMPLEXES*

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Abstract—The 5-sulphosalicylate complexes of Al(III), Cr(III), U(VI), Ni(II), Co(II) and Mn(II) have been investigated by the potentiometric method. The Al(III)– and U(VI)–5-sulphosalicylate systems were also investigated spectrophotometrically. It was found that Al(III) forms 1:1, 1:2 and 1:3 complexes at pH values of 3·8, 5·5 and 8·5, respectively and that U(VI) forms 1:1 and 1:2 complexes at pH values of 4·5 and 7·5, respectively. The stability constants for Be(II)– and Cu(II)–5-sulphosalicylate complexes have been recalculated. The log k values found by the potentiometric method for the step-wise stability constants are as follows: Al, 13·20, 9·63, 6·06; Cr, 9·56; U, 11·14, 8·06; Ni, 6·42, 3·82; Co, 6·13, 3·69; Mn, 5·24, 3·00; Be, 11·71, 9·10; Cu, 9·52, 6·93.

ANDERSON and co-workers investigated the 5-sulphosalicylate complexes of U(VI),[1] Al(III),[2] Ni(II)[3] and Cr(III)[4] and showed that each of the metal ions form a 1:1 complex in an acidic medium. These workers reported values for the dissociation constants of all the metal complexes. Using BJERRUM's[5] method, PERRIN[6] reported the stability constants (k_1 and k_2) of several metal complexes of salicylate and sulphosalicylate. BABKO[7] determined the dissociation constant ($1/k_2$) of the 1:1 aluminium (III)–salicylate complex by a displacement method using an iron(III)–salicylate complex as an indicator. In a similar manner, NANDA and ADITYA[8] determined the dissociation constant ($1/k_1'$) of the 1:1 aluminium(III)–5–sulphosalicylate complex at pH 2·4, using the mono (5-sulphosalicylate) iron(III) complex as an indicator. BABKO[7] observed a change in the ultra-violet absorption maxima of salicylic acid in the presence of aluminium ions, in the pH range 4·0–6·0.

In the present communication, an attempt has been made to calculate the step-wise stability constants of some metal complexes of 5-sulphosalicylic acid.

EXPERIMENTAL

Reagents. Iron-free 5-sulphosalicylic acid was used throughout this work. Reagent-grade nitrates of all metals were used except for aluminium (potassium alum) and manganese (chloride). All metal ion solutions were standardized by titration with standard ethylenedinitrilotetraacetic acid. Chromium nitrate solution was standardized by oxidation to chromate and titration with standard ferrous ammonium sulphate. Solutions of U(VI) were prepared by direct weighing of $UO_2(NO_3)_2 \cdot 6H_2O$.

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] R. T. FOLEY and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 909 (1949).
[2] M. B. LASATER and R. C. ANDERSON, *J. Amer. Chem. Soc.* **74**, 1429 (1952).
[3] M. B. LASATER and R. C. ANDERSON, *J. Amer. Chem. Soc.* **74**, 1431 (1952).
[4] A. M. LIEBMAN and R. C. ANDERSON, *J. Amer. Chem. Soc.* **74**, 2111 (1952).
[5] J. BJERRUM, *Metal Ammine Formation in Aqueous Solution*. P. Hasse, Copenhagen (1941).
[6] D. D. PERRIN, *Nature, Lond.* **182**, 741 (1958).
[7] A. K. BABKO and T. N. RYCHKOVA, *Zh. Obshch. Khim.* **18**, 1617 (1948); *Chem. Abstr.* **43**, 2536d (1949).
[8] R. K. NANDA and S. ADITYA, *J. Indian Chem. Soc.* **34**, 577 (1957).

Apparatus and procedure. The essential details of apparatus and procedure have been described in a preceding publication.[9] The experimental method consisted of potentiometric titration of 5-sulphosalicylic acid in the absence of and in the presence of the metal ions being investigated. The Al(III) and U(VI) complexes were also studied spectrophotometrically. All solutions were 0·1 M in sodium perchlorate.

Calculations. In the selection of data for computation of stability constants, a series of $\bar{n}$ and $[SSA^{3-}]$ values were calculated from each titration curve of a particular metal ion. The values of the

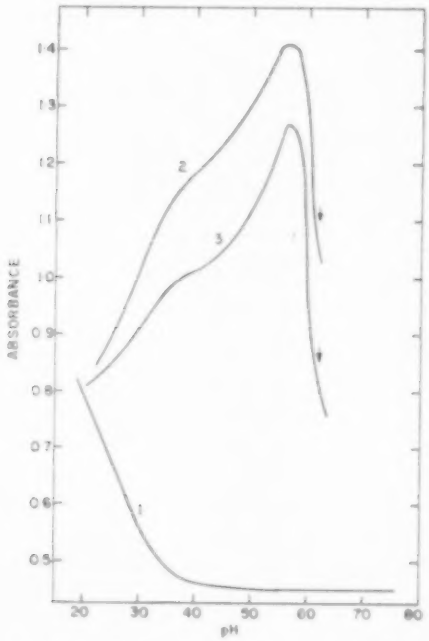

FIG. 1.—Effect of pH on absorbance at 315 mμ; curve 1, $5{\cdot}0 \times 10^{-4}$ M in H_3SSA; curve 2, $5{\cdot}0 \times 10^{-4}$ M in H_3SSA and $2{\cdot}5 \times 10^{-4}$ M in Al(III); curve 3, $5{\cdot}0 \times 10^{-4}$ M in H_3SSA and $1{\cdot}67 \times 10^{-4}$ M in Al(III). The absorbances were measured in 1·0 cm silica cells. The arrows indicate the pH at which precipitation occurred.

constants were obtained by solving $\bar{n}$ equations simultaneously. An attempt was made to select sets of data in such a manner that in each calculation of stability constants, all the stability constants were of significance.

An IBM 650 electronic digital computor was used in making all calculations.

ALUMINIUM(III)–5-SULPHOSALICYLATE COMPLEXES

Effect of pH. Fig. 1 shows the variation in absorbance with pH of solutions $5{\cdot}0 \times 10^{-4}$ M in H_3SSA (curve 1), $5{\cdot}0 \times 10^{-4}$ M in H_3SSA and $2{\cdot}5 \times 10^{-4}$ M in Al(III) (curve 2) and $5{\cdot}0 \times 10^{-4}$ M in H_3SSA and $1{\cdot}67 \times 10^{-4}$ M in Al(III) (curve 3), where H_3SSA is HO_3S–C_6H_3–OH–COOH. The absorbances were measured at 315 mμ, the wavelength at which the presence of Al(III) caused a maximum change in the absorbance of H_3SSA solutions. The absorbance of H_3SSA (curve 1) decreases as the pH increases and is almost constant in the pH range 4·0–9·0. The sharp rise in the absorbance of solutions containing H_3SSA and Al(III) (curves 2 and 3) above pH 2·0,

[9] C. V. BANKS and R. S. SINGH, *J. Amer. Chem. Soc.* **81**, 6159 (1959).

Vol. 15 1960

indicates the formation of a complex at about pH 3·8, which changes to a higher complex above pH 4·0. The higher complex hydrolyses completely above pH 6·0 as is indicated by a sharp decrease in absorbance. No evidence for the formation of a complex above pH 6·0 was observed because of this hydrolysis. The absorbance of the sulphosalicylate ion prevented the use of a sufficient amount of H_3SSA to repress the hydrolysis of the complex. The composition of the two complexes was determined by JOB's[10] method. The ratio of aluminium(III) to 5-sulphosalicylic acid was found to be 1:1 for the complex formed at pH 3·85, and 1:2 for the complex formed at pH 5·60. LASATER and ANDERSON[2], using the displacement method with mono(5-sulphosalicylate)–copper(II) complex as the indicator, reported that Al(III) forms a 1:1 complex with 5-sulphosalicylic acid at pH 4·10.

Stability constants (spectrophotometric). The procedure was similar to that previously described.[9] At a constant pH, the formation of the 1:1 aluminium(III)–5-sulphosalicylate complex can best be represented by the equation

$$Al^{3+} + HSSA^{2-} \leftrightharpoons AlSSA + H^{+}. \tag{1}$$

At pH 3·89, the uncomplexed 5-sulphosalicylate exists as H_2SSA^{-} and $HSSA^{2-}$. From equation (1), it follows that:

$$k_1'[H^+] = \frac{[AlSSA][H^+]}{[Al^{3+}][HSSA^{2-}]} = \frac{[AlSSA]Ka_3}{[Al^{3+}][SSA^{3-}]} = k_1 Ka_3 \tag{2}$$

where k_1 is the stability constant and Ka_2[11] and Ka_3[9] are the second and third dissociation constants of 5-sulphosalicylic acid, respectively.

At pH 3·89, it can be assumed that the absorbance of a solution of Al(III) and 5-sulphosalicylic acid at 315 mμ, is due to the AlSSA complex, the uncomplexed H_2SSA^{-} and $HSSA^{2-}$, and can be represented by the following equation:

$$A = l\left[\epsilon_0[AlSSA] + [HSSA^{2-}]\left(\frac{\epsilon_1 \cdot [H^+]}{Ka_2} + \epsilon_2\right)\right] \tag{3}$$

where ϵ_0, ϵ_1 and ϵ_2 are the molar absorptivities for AlSSA, H_2SSA^{-} and $HSSA^{2-}$, respectively. The value of ϵ_2 was determined from the observed absorbance and the known concentration of a solution containing only 5-sulphosalicylate at pH 5·5, a condition under which the predominate species is $HSSA^{2-}$. The value of ϵ_1 was calculated from equation (3), and values of Ka_2, ϵ_2 and the total 5-sulphosalicylate concentration for solutions containing only 5-sulphosalicylate at pH 3·89. The value of ϵ_0 was calculated from equation (3) in a manner similar to that used for ϵ_1 for solutions containing aluminium ions and an excess of 5 sulphosalicylate at pH 3·89. Considerable uncertainty is involved in the values of these molar absorptivities because the wavelength at which they were measured lies on the shoulder of the absorption band. The values of ϵ_0, ϵ_1 and ϵ_2, at 315 mμ, were found to be $3{\cdot}78 \times 10^3$, $2{\cdot}42 \times 10^3$ and 890, respectively.

For solutions containing a 1:1 mixture of Al(III) and 5-sulphosalicylic acid, in

[10] P. JOB, *Ann. Chim.* [10] **9**, 113 (1928).
[11] C. V. BANKS and J. H. PATTERSON, *J. Amer. Chem. Soc.* **73**, 3062 (1951).

which the total metal ion concentration is M_t and $[Al^{3+}] = [HSSA^{2-}] + [H_2SSA^-] = y$, and using Ka_2, one may write equations (2) and (3) as

$$k_1 = \frac{k_1'[H^+]}{Ka_3} = \frac{(M_t - y)([H^+] + Ka_2)[H^+]}{y^2 Ka_2 Ka_3} \text{ and} \tag{4}$$

$$A = l\left[\epsilon_0(M_t - y) + \frac{y(\epsilon_1[H^+] + \epsilon_2 Ka_2)}{[H^+] + Ka_2}\right]. \tag{5}$$

A stock solution of Al(III) and 5-sulphosalicylate, having a mole ratio of 1:1 was prepared and the pH adjusted to 3·89 with NaOH. Several dilutions, in the range (3·0–5·0) $\times 10^{-4}$ M in total Al(III), were prepared each being 0·1 M in $NaClO_4$ and 5·0 $\times 10^{-3}$ M in acetate buffer. The absorbance of each of these solutions was measured at 315 mμ. The value of y was calculated from equation (5), which when substituted into equation (4), gives a value of k_1 equal to (8·16 $\pm$ 0·25) $\times 10^{12}$.

NANDA and ADITYA[8] reported values of (1·72, 1·94 and 2·58) $\times 10^{-3}$ for the stepwise dissociation constant ($1/k_1'$) at pH 2·4 and at ionic strengths of 0·02, 0·05 and 0·2, respectively. Using the value for $1/k_1'$ at ionic strength 0·05 in equation (4), the value for k_1 was calculated to be 2·63 $\times 10^{12}$.

A similar procedure was used to calculate the stability constant for the 1:2 aluminium(III)–5-sulphosalicylate complex, which forms at about pH 5·58. A stock solution of the complex, having the mole ratio of 1:2, was prepared and the pH adjusted to 5·58 with NaOH. Several dilutions, in the range (1·0–2·5) $\times 10^{-4}$ M in total Al(III), were prepared, each being 0·1 M in $NaClO_4$ and 5·0 $\times 10^{-3}$ M in acetate buffer. The absorbance of each of these solutions was measured at 315 mμ.

For solutions at pH 5·58 which contain a 1:2 mixture of Al(III) and 5-sulphosalicylate, and in which the total metal ion concentration is M_t and $[AlSSA] = [HSSA^{2-}] = y$, one may write

$$k_2' = \frac{[Al(SSA)_2^{3-}]}{[AlSSA][HSSA^{2-}]} = \frac{M_t - y}{y^2} = \frac{k_2 Ka_3}{[H^+]} \text{ and} \tag{6}$$

$$A = l[y(\epsilon_0 + \epsilon_2) + \epsilon_3(M_t - y)] \tag{7}$$

where ϵ_3 is the molar absorptivity of $Al(SSA)_2^{3-}$. The value of ϵ_3 was calculated from equation (7), assuming that no AlSSA complex was present. This value was then adjusted until consistent values of k_2 were obtained. The final value of ϵ_3 was 7·20 $\times 10^3$. The value of y can be calculated from equation (7) which when substituted in equation (6) gives a value of k_2 equal to (1·03 $\pm$ 0·36) $\times 10^{10}$.

Potentiometric titrations. Fig. 2 represents the titration of 100 ml of solutions 2·503 $\times 10^{-2}$ M in H_3SSA (curve 1), 2·503 $\times 10^{-2}$ M in H_3SSA and 1·25 $\times 10^{-3}$ M in $AlK(SO_4)_2$ (curve 2), and 2·503 $\times 10^{-2}$ M in H_3SSA and 2·50 $\times 10^{-3}$ M in $AlK(SO_4)_2$ (curve 3) with 0·1000 M NaOH. Curve 1 shows an inflexion when about two equivalents of base per mole of H_3SSA have been added, indicating that only two protons of H_3SSA are displaced. In the presence of Al(III) (curves 2 and 3), the phenolic proton of H_3SSA is also displaced due to complex formation, as is indicated by the additional amount of base consumed by these solutions. This additional amount of base gives directly the amount of H_3SSA complexed with Al(III). Curves 2 and 3 have an inflexion at about pH 9·0, which occurs when approximately three

Vol. 15 1960

equivalents of base per mole of Al(III) have been added. This shows that a 1:3 complex is formed at high pH and only in the presence of a large excess of H_3SSA. No visible evidence of hydrolysis of the complex was observed during the titrations but solution 3 (ratio of 10 H_3SSA to 1 Al(III), curve 3) hydrolysed a few hours after the titration was completed. The reactions may be represented as:

$$H_3SSA + 2OH^- \leftrightharpoons HSSA^{2-} + 2H_2O \quad (8)$$

$$Al^{3+} + HSSA^{2-} + OH^- \leftrightharpoons AlSSA + H_2O \quad (9)$$

$$AlSSA + HSSA^{2-} + OH^- \leftrightharpoons [Al(SSA)_2]^{3-} + H_2O \quad (10)$$

$$[Al(SSA)_2]^{3-} + HSSA^{2-} + OH^- \leftrightharpoons [Al(SSA)_3]^{6-} + H_2O. \quad (11)$$

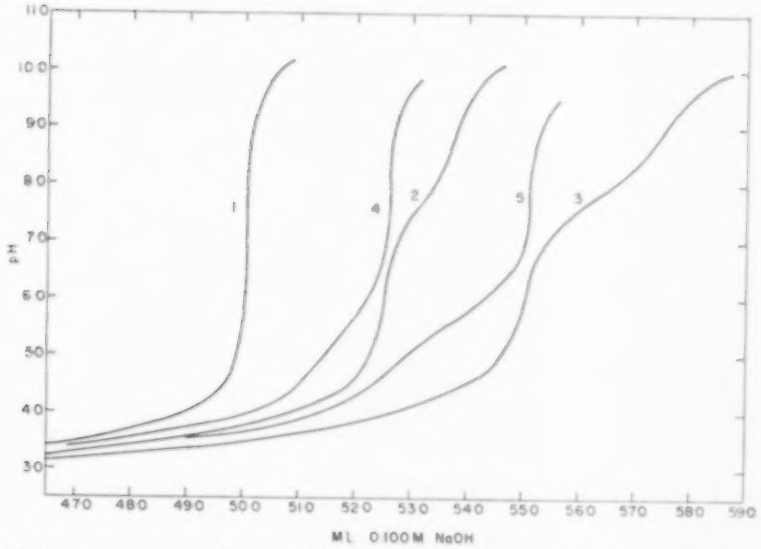

FIG. 2.—Potentiometric titration of 5-sulphosalicylic acid in the presence of Al(III) and U(VI): curve 1, $2{\cdot}503 \times 10^{-2}$ M in H_3SSA; curve 2, $2{\cdot}503 \times 10^{-2}$ M in H_3SSA and $1{\cdot}25 \times 10^{-3}$ M in Al(III); curve 3, $2{\cdot}503 \times 10^{-2}$ M in H_3SSA and $2{\cdot}50 \times 10^{-3}$ M in Al(III); curve 4, $2{\cdot}503 \times 10^{-2}$ M in H_3SSA and $1{\cdot}25 \times 10^{-3}$ M in U(VI); curve 5, $2{\cdot}503 \times 10^{-2}$ M in H_3SSA and $2{\cdot}50 \times 10^{-3}$ M in U(VI).

Stability constants (potentiometric). The procedure used for measuring the stepwise stability constants of the aluminium(III)–5-sulphosalicylate complexes was similar to that described in a previous publication.[9] The evaluation of $\bar{n}$ values was made from Fig. 2. At any pH above 3·5, the horizontal distance between curve 1 and curve 2, or curve 3, measures quite accurately the additional base consumed by reactions (8)–(11) or the total number of moles of 5-sulphosalicylate complexed. This number divided by the total Al(III) concentration is $\bar{n}$. At any pH, the concentration of SSA^{3-} was calculated from the known dissociation constants (Ka_2 and Ka_3) of 5-sulphosalicylic acid. The lowest value of $\bar{n}$ that could be obtained was 1·14 and hence the value of k_1 was computed from the fact that at $\bar{n} = 1{\cdot}5$, $-\log [SSA^{3-}] = \frac{1}{3} \log K$ or $\frac{1}{3} \log k_1k_2k_3$. The approximate values of $\log k_2$ and $\log k_3$ were known from the $\bar{n}$ curve, thus making it possible to obtain a value for $\log k_1$. Using experimental

values of $\bar{n}$ and [SSA^{3-}] and various values of k_1, the values of k_1k_2 and $k_1k_2k_3$ were computed by solving two simultaneous $\bar{n}$ equations. The results are given in Table 1.

URANIUM(VI)–5-SULPHOSALICYLATE COMPLEX

Fig. 3 represents the changes in absorbance at 450 mμ with pH of solutions containing uranium(VI) nitrate and H_3SSA in the ratios of 1:2 (curve 1), 1:6 (curve 2) and

TABLE 1.—STABILITY CONSTANTS FOR VARIOUS METAL–5-SULPHOSALICYLATE COMPLEXES*

Metal ion	This work			Previous work					
	log k_1	log k_2	log k_3	$1/k_1'$	pH	Ionic strength	pKa_3	log k_1†	Ref.
Al(III)	13·20	9·63	6·06	$1·94 \times 10^{-3}$	2·40	0·05	12·11	12·42	8
	12·91‡	10·01‡		$5·00 \times 10^{-4}$	4·10	0·05 (approx.)	12·11	11·31	2
U(VI)	11·14	8·06		$1·93 \times 10^{-4}$	4·65	0·02	12·28	11·31	1
Cr(III)	9·56	ppt.		$1·00 \times 10^{-3}$	5·00	0·30	11·95 (est.)	9·95	4
Ni(II)	6·42	3·82							
Co(II)	6·13	3·69							
Mn(II)	5·24	3·00							
Be(II)**	11·71	9·10							
	11·72‡	8·88‡							
Cu(II)**	9·52	6·93		$2·0 \times 10^{-9}$	5·00	0·05	12·11	9·81	12

* Temperature 25°; $pKa_2 = 2·49$; $pKa_3 = 12·00$ both at $\mu = 0·1$. The ionic strength varied from 0·1 to 0·15 during the potentiometric titrations.

† The values of k_1 were calculated by means of equation (2), from values reported in the literature which were assumed to be values of $1/k_1$.

‡ These values were determined by the spectrophotometric method; all other values were determined by the potentiometric method.

** Recalculated[9] log k values obtained by solving two $\bar{n}$ equations simultaneously with the help of IBM 650 electronic computor, using $pKa_3 = 12·00$ instead of 11·74.

1:10 (curve 3). Curve 1 shows an increase in absorbance with increasing pH, reaching a maximum at pH 4·8 after which it decreases sharply as hydrolysis of the complex takes place. Curve 2 is similar to curve 1 up to pH 4·5 after which the absorbance, instead of decreasing, increases and remains constant in the pH range 6·8–7·2, then decreases sharply due to the hydrolysis of the complex. Curve 3 is identical to curve 2 except that the increase in absorbance above pH 4·5 is more pronounced and remains constant in the pH range 7·0–8·4 and that the hydrolysis occurs only above pH 9·2. FOLEY and ANDERSON[11] have shown that at pH 4·65, U(VI) forms a 1:1 complex with 5-sulphosalicylate. The increase in absorbance observed in curves 2 and 3 after pH 4·5, indicates the formation of another complex, which forms at pH 7·0–8·5 only in the presence of a large excess of H_3SSA. The composition of this complex could not be determined by JOB's method because of the hydrolysis of the complex.

Stability constant (potentiometric). Fig. 2 represents the titration of 100 ml of solutions $2·503 \times 10^{-2}$ M in H_3SSA (curve 1), $2·503 \times 10^{-2}$ M in H_3SSA and $1·25 \times 10^{-3}$ M in $UO_2(NO_3)_2$ (curve 4) and $2·503 \times 10^{-2}$ M in H_3SSA and $2·50 \times 10^{-3}$ M in

[12] S. E. TURNER and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 912 (1949).

Vol. 15 1960

$UO_2(NO_3)_2$ (curve 5) with 0·1000 M NaOH. Curve 1 has one inflexion at about two equivalents of base per mole of 5-sulphosalicylate (equation 8). Curves (4) and (5) have an inflexion when about two equivalents of base per mole of U(VI) have been added. The reactions can be represented as

$$UO_2^{2+} + HSSA^{2-} + OH^- \leftrightharpoons UO_2SSA^- + H_2O \quad (12)$$

$$UO_2SSA^- + HSSA^{2-} + OH^- \leftrightharpoons UO_2(SSA)_2^{4-} + H_2O. \quad (13)$$

The additional two equivalents of base consumed indicate the formation of a 1:2

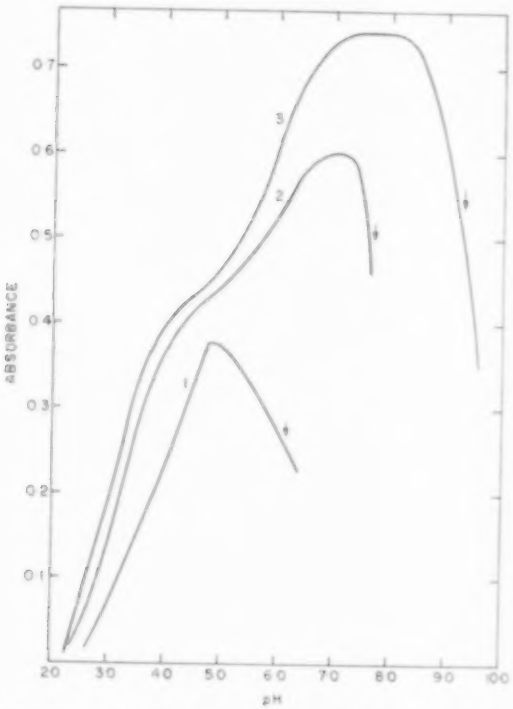

FIG. 3.—Effect of pH on absorbance at 450 mμ; curve 1, $5{\cdot}0 \times 10^{-4}$ M in U(VI) and $1{\cdot}0 \times 10^{-3}$ M in H_3SSA; curve 2, $5{\cdot}0 \times 10^{-4}$ M in U(VI) and $3{\cdot}0 \times 10^{-3}$ M in H_3SSA; curve 3, $5{\cdot}0 \times 10^{-4}$ M in U(VI) and $5{\cdot}0 \times 10^{-3}$ M in H_3SSA. The absorbances were measured in 2·0 cm cells. The arrows indicate the pH at which precipitation occurred.

complex as the pH is raised. No hydrolysis of the complex occurred during the titration, but solution 3 (curve 5) was observed to hydrolyse a few hours after the titration was completed.

The stability constants were calculated from $\bar{n}$ and $[SSA^{3-}]$ values. A series of values of $\bar{n}$ and $[SSA^{3-}]$ were obtained from Fig. 2 (curves 1 and 4 or 5) and were used to solve for k_1 and k_1k_2. The values of the constants are given in Table 1.

FOLEY and ANDERSON[1] have calculated the dissociation constant ($1/k_1'$) of the 1:1 uranium(VI)–5-sulphosalicylate complex. At pH 4·65 and $\mu = 0{\cdot}015$, the value was found to be $1{\cdot}93 \times 10^{-4}$. The value of k_1 was calculated from this value of $1/k_1'$ by means of equation (4) and was found to be $2{\cdot}19 \times 10^{11}$. This value is close to the value of k_1 obtained in this study by the potentiometric method.

Ni(II)-, Co(II)-, Mn(II)- AND Cr(III)-5-SULPHOSALICYLATE COMPLEXES

Fig. 4 represents the titration of 100 ml of solutions $2{\cdot}500 \times 10^{-2}$ M in H_3SSA (curve 1), $2{\cdot}500 \times 10^{-2}$ M in H_3SSA and $2{\cdot}500 \times 10^{-3}$ M in $Ni(NO_3)_2$ (curve 2), $2{\cdot}500 \times 10^{-2}$ M in H_3SSA and $2{\cdot}500 \times 10^{-3}$ M in $MnCl_2$ (curve 4) and $2{\cdot}515 \times 10^{-2}$ M in H_3SSA and $2{\cdot}500 \times 10^{-3}$ M in $Cr(NO_3)_3$ (graph not included in Fig. 4) with 0·1000 M NaOH. From Fig. 4 it is evident that the complex formation takes place only

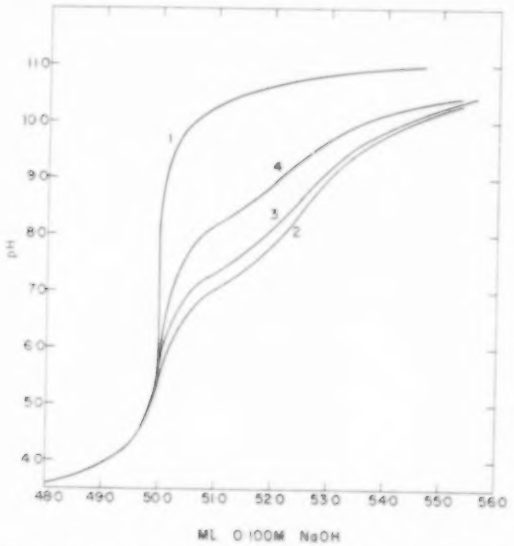

FIG. 4.—Potentiometric titration of 5-sulphosalicylic acid in the presence of Ni(II), Co(II) and Mn(II): curve 1, $2{\cdot}50 \times 10^{-2}$ M in H_3SSA; curve 2, $2{\cdot}50 \times 10^{-2}$ M in H_3SSA and $2{\cdot}50 \times 10^{-2}$ M in Ni(II); curve 3, $2{\cdot}50 \times 10^{-2}$ M in H_3SSA and $2{\cdot}50 \times 10^{-2}$ M in Co(II); curve 4, $2{\cdot}50 \times 10^{-2}$ M in H_3SSA and $2{\cdot}50 \times 10^{-2}$ M in Mn(II).

above pH 6·0, except for chromium, which forms above pH 3·5. The chromium, cobalt and manganese complexes hydrolyse at pH 5·8, 10·7 and 10·1, respectively, whereas the nickel complex does not hydrolyse up to pH 10·9.

The stability constants of the complexes were calculated from $\bar{n}$ and $[SSA^{3-}]$ values obtained from Fig. 4. The values of the constants are given in Table 1. Due to the hydrolysis of the manganese and chromium complexes, $\bar{n}$ values above 1·2 could not be obtained and it is doubtful whether these metals form higher complexes with 5-sulphosalicylate. LASATER and ANDERSON[3] and LIEBMAN and ANDERSON[4] have reported that 5-sulphosalicylate forms a 1:1 complex with nickel and chromium ions at pH of 7·5 and 5·0, respectively.

Vol. 15 1960

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MOLYBDIC ACID AND ITS ORGANIC COMPLEXES—IV

COMPLEXES OF MOLYBDATE WITH POLYHYDRIC PHENOLS—A SPECTROPHOTOMETRIC STUDY

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Abstract—The molybdate ion in aqueous solution forms intense yellow to orange-brown complexes with polyhydric phenols. Using a spectrophotometric method it is shown that at pH 7 the ratio of polyhydric phenol to molybdate in the complex is 2 : 1. At lower pH values the composition of the complexes becomes variable, and changes according to the other substituent groups on the aromatic nucleus. Only the catechol complex retains a constant composition over the pH range studied. The complexes of six phenols are examined: catechol, protocatechuic acid, 4-methylcatechol, Tiron, pyrogallol and gallic acid. The complex formed with salycilic acid is examined for comparison.

THE reaction between acidified molybdate solutions and phenols has been known for a long time.[1,2] Catechol and related compounds (in which there are at least two ortho hydroxyl groups) yield yellow to orange-brown complexes with molybdate solutions. This reaction does not take place with polyhydric phenols in which the hydroxyl groups are placed in meta or para positions to each other.[3,4] Since aliphatic polyhydroxy compounds, with the hydroxyl groups on adjacent carbon atoms form colourless complexes with molybdate,[5] it appears that the formation of coloured complexes is due to the aromatic nucleus. Some quantitative work on the nature and empirical formulae of the complexes formed by polyhydric phenols with other ions has been reported,[6,7] and particularly noteworthy are the contributions of YOE[8] and SOMMER[3] on the complexes formed by Fe^{3+} and Ti^{4+} with Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) and catechol. Apart from a short note,[9] various analytical applications[10,11,12] and a recent communication by us,[13] very little quantitative data seems to be available for the molybdenum complexes. The situation with molybdenum is more complicated since the reaction is with the molybdate anion and not with a cation as in the other complexes. The orange-yellow colours produced, however, are

[1] D. H. KILLEFER and A. LINZ, *Molybdenum Compounds* pp. 198–199. Interscience, New York (1952).
[2] L. FERNANDES, *Gazz. Chim. Ital.* **55**, 424 (1925).
[3] L. SOMMER, *Coll. Czech. Chem. Comm.* **22**, 414, 1793 (1957).
[4] A. T. CASEY and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **10**, 58 (1959).
[5] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 273 (1959).
[6] D. D. PERRIN, *Nature, Lond.* **182**, 741 (1958).
[7] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN, *Stability Constants—Part I. Organic Ligands.* Chemical Society Special Publication No. 6, London (1957).
[8] J. H. YOE and A. L. JONES, *Industr. Engng. Chem. (Anal.)* **16**, 111 (1944).
[9] J. C. MCGOWAN and P. W. BRIAN, *Nature, Lond.* **159**, 373 (1947).
[10] S. SEIFTER and B. NOVIC, *Analyt. Chem.* **23**, 188 (1951).
[11] F. WILL and J. H. YOE, *Analyt. Chim. Acta* **8**, 546 (1953).
[12] S. YA SCHNAIDERMAN and I. B. ROBEROVA *Analyt. Abstr.* **6**, No. 18 (1959).
[13] H. BUCHWALD and E. RICHARDSON, *Chem. & Ind.* 753 (1959).

particularly suitable for spectrophotometric studies.[11] In this paper the spectrophotometric studies with six polyhydric phenols are reported: catechol, 4-methylcatechol protocatechuic acid (3,4-dihydroxybenzoic acid), Tiron, pyrogallol and gallic acid.

EXPERIMENTAL

Standard solutions of sodium molybdate were prepared from an analysed batch of solid. Stock solutions 0·1 M and 0·02 M in Na_2MoO_4 were generally used.

All the phenols used were obtained commercially, in the analytical reagent grade whenever possible. Where the analytical reagent grade was unavailable the materials were recrystallised from a suitable solvent. Aqueous stock solutions 0·02 M and 0·05 M were prepared as required, but were not kept for any appreciable time since discoloration occurred in most cases after only a few hours.

Sodium acetate was used as a semi-buffer solution and to maintain a relatively constant ionic strength.

A solution of perchloric acid was generally used to adjust the pH. A stock solution approximately 1·4 M was prepared from the A.R. grade 60 per cent acid.

The working solutions on which measurements were carried out were prepared from suitable quantities of the above reagents and kept in well stoppered flasks. pH measurements were made with a glass–calomel electrode system calibrated to read 4·00 at 20°C with 0·05 M potassium hydrogen phthalate. This calibration was checked at pH 7·00 with a boric acid–sodium borate buffer and at pH 2·54 with 0·01 M potassium tetroxalate. Suitable glass electrodes were available for solutions of low and high pH values.

Conductivity measurements were made on a Mullard conductivity bridge operating in the most sensitive range, with a maximum error of ±2%. A rigid dip-type cell having a constant 1·54 was used; this cell could be sealed into the reaction vessel where necessary in order to minimize atmospheric oxidation.

The spectrophotometric work was carried out in 1 cm cuvettes using Unicam SP 500 and Hilger Uvispek spectrophotometers. All measurements were made at 20 ± 2°C. A thermostatic cell carrier was available for the Unicam spectrophotometer but was not used since a preliminary investigation showed that a temperature fluctuation of ±5°C had no significant effect.

Vol. 15 1960

RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of the complexes obtained with the six phenols under similar conditions. The percentage transmission curve is used since it emphasizes the differences. With all the phenols except Tiron the maximum absorption occurs at a wavelength of about 400 mμ. At wavelengths below 400 mμ no definite peaks are found in the curves, only a broad absorption band. It will be noted that the absorption spectra of the catechol, 4-methylcatechol and protocatechuic acid complexes are practically identical. At any particular wavelength, the introduction of two strongly deactivating $—SO_3Na$ groups into the aromatic nucleus lowers the absorption appreciably.

This effect is less marked at the extremities of the curves. The absorption increases on the introduction of a third *ortho*-hydroxyl group. It would appear therefore, that deactivating groups tend to decrease the optical density whilst activating groups have the opposite effect.

Table 1 shows the variation in optical density using increasing concentrations of molybdate in presence of a large excess of the phenols. Fig. 2, which is a typical example, indicates that Beer's law holds for all the systems. A comparison of the results under these conditions (i.e. in sufficient excess of phenol to ensure complete complexing of the molybdate), shows that a variation of the substituent groups on the aromatic nucleus causes little change in the optical density or visual colour of the complexes. This indicates that the transition of electrons which gives rise to the colour

of the complex is centred around the molybdate anion. The colour reaction is sensitive to relatively small concentrations of molybdate and lends itself ideally to analytical applications.

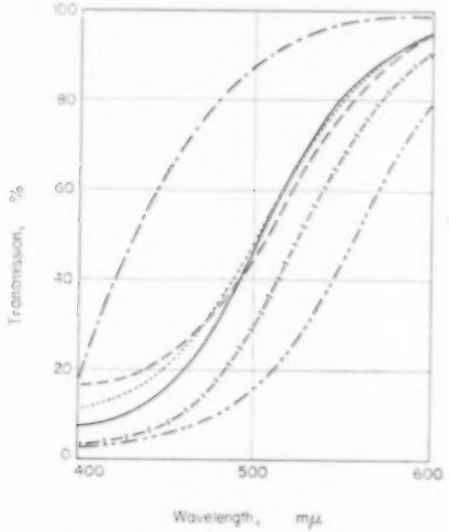

FIG. 1.—Solutions 0·1 M in sodium acetate, 0·01 M in sodium molybdate and 0·001 M in polyhydric phenol.

– · – · – · – Tiron
– – – 4-methylcatechol
. . . . . catechol
——— protocatechiuc acid
– | – | – gallic acid
– " – " – pyrogallol

TABLE 1.—VARIATION OF OPTICAL DENSITY WITH MOLYBDATE CONCENTRATION FOR SOLUTIONS 0·02 M IN SODIUM ACETATE AND 0·015 M IN POLYHYDRIC PHENOL.

$NaMoO_4$ ($M \times 10^4$)	0	0·2	0·4	0·6	0·8	1·0
Phenol	Optical densities at 450 mμ					
Catechol	0·02	0·09	0·16	0·23	0·30	0·37
4-methycatechol	0·02	0·10	0·18	0·26	0·34	0·41
Protocatechuic acid	0·02	0·09	0·17	0·25	0·33	0·40
Tiron	0·03	0·10	0·18	0·26	0·34	0·42
Pyrogallol	0·04	0·12	0·19	0·28	0·34	0·42
Gallic acid	0·02	0·09	0·16	0·24	0·32	0·39

The coloured complexes are formed immediately, and do not change with temperature in the region 10°–40°C, although at temperatures near to the boiling point there is a reversible bleaching effect. The orange-yellow colours formed in neutral solutions with catechol and pyrogallol degenerate within a few hours to a muddy brown due to oxidation. With protocatechuic acid and 4-methylcatechol this oxidation

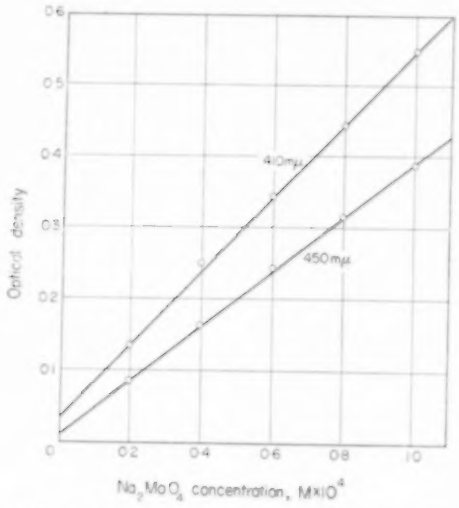

FIG. 2.—Applicability of Beer's Law for the gallic acid–molybdate system.
Solutions 0·02 M in sodium acetate.
0·015 M in gallic acid.
And containing various concentrations of sodium molybdate

Vol. 15 1960

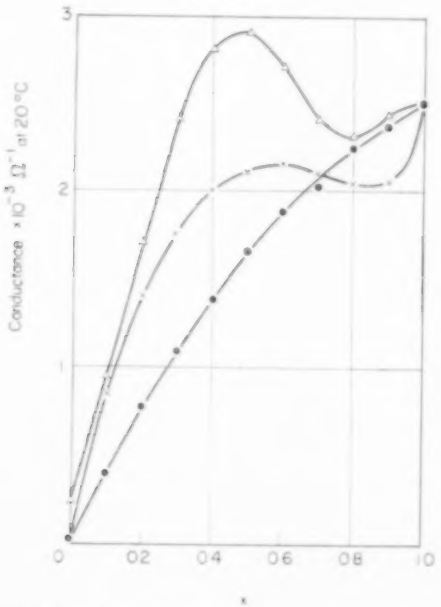

FIG. 3.—● = resorcinol, hydroquinane } identical with simple molybdic acid–water solution.
× = pyrogallol
△ = gallic acid.
x = Mole fraction molybdic acid, where [phenol] + [molybdic acid] = 0·0425 molar.

takes somewhat longer. With gallic acid the colour remains unchanged for two or three days whilst with Tiron the colour is completely stable. All the stock solutions of the phenols, though colourless at first, turn yellow to pink in colour within periods ranging from a few hours to several days, depending on the ease of atmospheric oxidation.

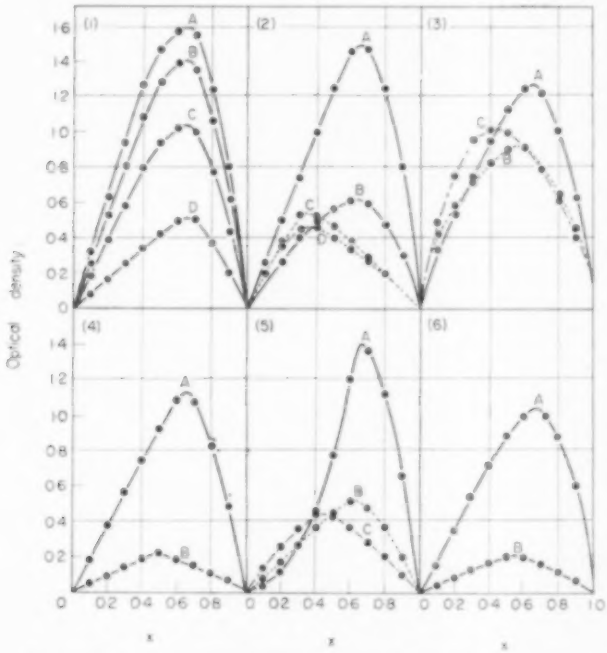

FIG. 4.—X = Mole fraction of polyhydric phenol such that [phenol] + [molybdate] = 0·01 molar. Solutions 0·05 M in sodium acetate.
Optical densities at 20° C and various wavelengths.
1—Catechol at 480 mμ. *A*—pH 5·0; *B*—pH 4·0; *C*—pH 3·0; *D*—pH 2·0.
2—Gallic acid at 530 mμ. *A*—pH 5·4–6·4; *B*—pH 4·2; *C*—pH 1·8; *D*—pH 1·3.
3—Pyrogallol at 550 mμ. *A*—pH 7·0; *B*—pH 4·4; *C*—pH 1·9.
4—Protocatechuic acid at 530 mμ. *A*—pH 5·3–6·3; *B*—pH 1·7.
5—Tiron at 520 mμ. *A*—pH 6·5–7·5; *B*—pH 4·1; *C*—pH 1·8.
6—4-methylcatechol at 530 mμ. *A*—pH 7·0; *B*—pH 1·8.

In order to determine the composition of the complexes a conductometric method of continuous variations, similar to that used in previous studies, was tried in the first instance. Fig. 3 shows the curves obtained using various phenols in conjunction with pure molybdic acid (prepared by an ion-exchange technique).[5] The curve for the resorcinol–molybdic acid and the hydroquinone–molybdic acid systems is the same as that obtained for molybdic acid on its own. The other curves shown are those for the pyrogallol and gallic acid systems. The curve for catechol (not shown) is similar to that for pyrogallol. Although complex formation is indicated for the last three phenols mentioned, no definite information can be gained about the composition of the complexes.

JOB'S[14] method of continuous variations for the systems was investigated and the curves obtained are shown in Fig. 4. The spectrophotometric measurements were

[14] P. JOB, *Ann. Chim.* **6**, 97 (1935).

carried out at various pH values ranging from one to seven. In the pH region from four to seven all the phenols form complexes with a phenol to molybdate ratio of 2 : 1. The results at lower pH values are more varied. With catechol there is no

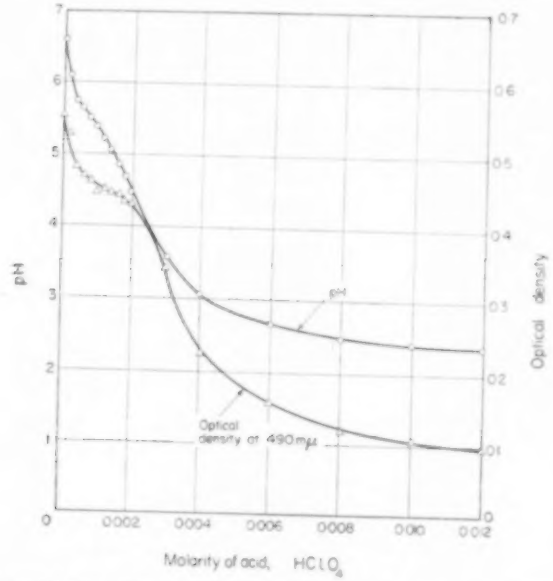

FIG. 5.—pH and optical density variation with molarity of acid present.
Solutions: 0·002 M in sodium molybdate
0·002 M in catechol.

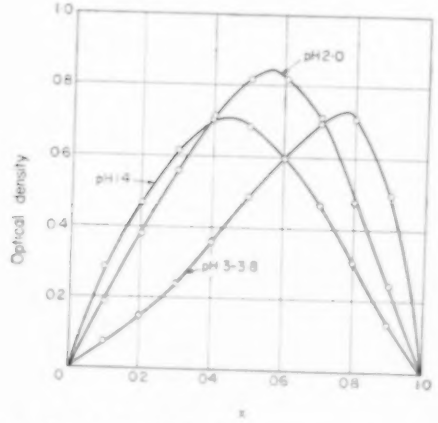

FIG. 6.—x = mole fraction of salicyclic acid.
[molybdate] + [salicyclic acid] = 0·02 molar.
Solutions 0·05 molar in sodium acetate.
Optical densities at 20°C.

change in complex composition as pH is lowered, but all the other phenols show considerable variation. At pH 2 the gallic acid and pyrogallol complexes appear to have a phenol to molybdate ratio of 1 : 2, whilst with the remaining phenols the

Vol. 15 1960

composition varies according to the substituent groups. Comparing the "pH/acid added" and the "optical density/acid added" curves for catechol (Fig. 5), although the composition does not change, it appears that the complex formation is dependent in some way on the state of aggregation of the molybdate anion. Further work is obviously necessary to elucidate the change in composition of the complexes with varying acidity. Colorimetric work in the alkaline range has not been attempted because of the gross interference by other coloured products. In analytical work the interference by coloured oxidation products can be eliminated by the addition of a conventional stabiliser such as sodium sulphite.[11]

For comparison, Fig. 6 shows similar curves for the molybdate–salicylic acid complex. At pH 7 the solutions are colourless, it is only on acidification that a pale yellow colour is formed. In order to obtain comparable optical densities a wavelength of 375 mμ was used. Lower wavelengths could not be used due to interference by the molybdate absorption band. It is evident that a different series of complexes is formed.

When an 0·1 M solution of catechol was added to 50 ml of 0·1 M sodium molybdate there was a steady rise in pH from a value of 6·95 to a maximum of 7·35 when approximately 20 ml of catechol solution had been added. A further addition of 20 ml produced a steady fall in pH of 0·1 unit. This rise in pH on addition of a weak acid indicates that hydroxyl ions are liberated during complex formation, which probably occurs as follows:

$$2C_6H_4(OH)_2 + Na_2MoO_4 \rightleftharpoons (MoO_4(C_6H_4)_2)^{2+} + 2\,Na^+ + 4\,OH^-$$

Further work on the phenols mentioned and on others is in progress and will be reported in due course.

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ANION EXCHANGE STUDIES—XXX

A NUMBER OF ELEMENTS IN ETHYLENEDIAMINETETRAACETIC ACID SOLUTIONS*[1]

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(*Received* 14 *October* 1959)

Abstract—Adsorbabilities of a number of metals (Be, Ca, Sr, Ba, Ra, Sc, V, Cr, Mn, Co, Ni and Zn) in EDTA solutions were studied as a function of EDTA concentration, supporting electrolyte concentration (NH_4Cl) and pH. Applicability of the results to separations is discussed and illustrations of several separations are given.

Adsorbability of EDTA by the chloride form of the exchanger was determined as a function of loading. The selectivity of the exchanger for EDTA is sufficiently low to permit separations in EDTA solutions with the resin remaining substantially in the chloride form. From measurement of distribution coefficients of metals as a function of EDTA and chloride concentration, the charges of a number of EDTA complexes was verified. Adsorbabilities as a function of pH at constant EDTA and supporting electrolyte concentrations were consistent with published constants for metal–EDTA equilibria. The stability constant for the EDTA complex of Ra(II) was estimated from the anion exchange data to be $10^{7.4}$.

Vol.
15
1960

DURING the last few years, extensive information has accumulated on the anion exchange behaviour of metals in a number of media. Particular attention has been given to chloride media, especially hydrochloric acid solutions, and information is available on the anion exchange behaviour of most metals in the periodic table over a broad range of hydrochloric acid concentrations.[2] From an inspection of these data it is evident that separation of metals from each other, either in groups or individually, is feasible by proper control of hydrochloric acid concentration.

However, a large number of elements (the alkali metals, the alkaline earths, many elements of Group III, as well as Ni(II), Cr(III) and Th(IV)) are not adsorbed at any hydrochloric acid concentration. These elements would therefore appear as a single large group in any separations scheme based on anion exchange in hydrochloric acid. Additional complexing agents are needed for their separation, and the present paper deals with the possible use of ethylenediaminetetraacetic acid and of its ions (to be abbreviated as EDTA or $H_nY^{(n-4)}$). This reagent was chosen since it is an excellent complexing agent and since quantitative information is available regarding its equilibria with a large number of metal ions.[3]

* This document is based on work performed for the U.S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by the Union Carbide Corporation. Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Memphis, Tennessee, November, 1956, and at the Spring American Chemical Society Meeting, Miami, Florida, 1957.

‡ Chemistry Department, Emory University, Atlanta 22, Georgia. Summer Employee, Oak Ridge National Laboratory, Chemistry Division, Summer 1956.

[1] Previous papers: (a) XXVII, F. NELSON, R. M. RUSH and K. A. KRAUS, *J. Amer. Chem. Soc.* **82**, 339 (1960); (b) XXVIII, F. NELSON, *J. Polymer Sci.* **40**, 563 (1959); and (c) XXIX, F. NELSON and K. A. KRAUS, *J. Chromatography* **3**, 279 (1960).

[2] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, pp. 113, 131. United Nations (1956).

[3] See e.g., *Stability Constants* Part I, compiled by J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN, The Chemical Society, London (1957)

EDTA solutions have been used extensively for cation exchange separations,[4] particularly of rare earths and actinides and for some anion exchange experiments. SAMUELSON and coworkers [5] used EDTA for separation of alkaline earths from alkali metals by anion exchange; NELSON[6] used it for the separation of some alkali metals from each other and KRAUS and NELSON[2] for the separation of alkaline earths from rare earths. More recently Schoenfeld and coworkers[7] presented extensive studies in EDTA for Sr(II), Pb(II), Y(III), Bi(III), and Th(IV).

From these studies, it appears that EDTA is a generally useful ligand with which fractionation by anion exchange of most metallic elements becomes feasible and the present paper summarizes our results for typical elements of the "HCl-non-adsorbable" group as well as for a few other elements.

EXPERIMENTAL

1. *Resin.* As in our earlier studies with EDTA solutions,[2,6] the experiments were carried out with a 4 per cent divinyl benzene quaternary amine polystyrene resin (Dowex-1, 80–100 mesh). Low cross-linking was chosen to decrease possible complications from unfavourable diffusion rates. Capacity, determined by titrating chloride ions displaced on treating a weighed amount of chloride-form resin with excess 1 M HNO_3, was 3·72 equivalents per kilogram dry resin (dried over "Anhydrone" at 60°C in a vacuum desiccator).

In some experiments the resin was used in the H_2Y^{2-} form, prepared by treating the chloride form with a large excess of 0·25 M Na_2H_2Y solution (pH ca. 4·6) followed by washing with a small amount of water. Although this treatment did not completely displace the chloride ions, the resin was sufficiently converted to the H_2Y^{2-} form for present purposes.

2. *Adsorbabilities.* Adsorbabilities were determined by column and equilibration methods at 25 ± 1°C. For the "standard" column method an aliquot of a solution containing the element of interest was added to a resin column previously pretreated with the same EDTA-supporting electrolyte solution with which elution was to be carried out. The effluent was analysed and the volume distribution coefficient D_v (amount adsorbed per litre of bed/amount per litre of solution) determined from the number of column volumes (V_{max}) at which the element appeared in maximum concentration. The fractional interstitial volume (i) necessary for computation of D_v ($D_v = V_{max} - i$) was determined by weighing the liquid removed on centrifuging (20 min) a "wet" column of resin of known volume. A small correction was made for the liquid adhering to the beads after centrifugation Assuming this value to be 3 per cent of the column volume,[8] i was found to be 0·38.

When distribution coefficients were large ($D_v > 10$), adsorbabilities were usually determined by batch equilibrations. Measured amounts of solution and resin were shaken at least overnight which appeared sufficient time for equilibration. From the change in metal concentration and the amount of resin and solution used, the weight distribution coefficient D (amount per kilogram dry resin/amount per litre solution) was computed. Conversion between D_v and D can be carried out if the bed density (ρ) is known ($D_v = D_\rho$). The bed density was found to range from 0·25 to 0·28 g dry resin per litre of bed for the 4 per cent D.V.B. resin in 0·01 to 2·0 M NH_4Cl.

In the case of Be(II), it was desired to obtain measurements under conditions where D is large and where the EDTA concentration of the solution is low and constant. A special column technique

[1] See e.g. (a) M. HONDA, *Japan Analyst* **3**, 132 (1953); *Chem. Abstr.* **48**, 9868 (1954); (b) S. W. MAYER and E. C. FREILING, *J. Amer. Chem. Soc.* **75**, 5647 (1953); (c) F. H. SPEDDING, J. E. POWELL and E. E. WHEELWRIGHT, *J. Amer. Chem. Soc.* **76**, 612 (1954); (d) R. BOVY and G. DUYCKAERTS, *Anal. Chim. Acta* **11**, 134 (1955); (e) J. LORIERS, *C. R. Acad. Sci., Paris* **240**, 1537 (1955); (f) F. W. CORNISH, G. PHILLIPS and A. THOMAS, *Canad. J. Chem.* **34**, 1471 (1956); (g) J. FUGER, *Bull. Soc. Chim. Belg.* **66**, 151 (1957); (h) M. N. NADKARNI, M. S. VARDE and V. T. ATHAVALE, *Anal. Chim. Acta* **16**, 421 (1957); (i) J. S. FRITZ and G. R. UMBREIT, *Anal. Chim. Acta* **19**, 509 (1958); (j) P. S. DAVIS, *Nature, Lond.* **183**, 674 (1959).

[2] (a) O. SAMUELSON and E. SJÖSTRÖM, *Analyt. Chem.* **26**, 1908 (1954); (b) O. SAMUELSON, E. SJÖSTRÖM and S. FORSBLOM, *Z. Anal. Chem.* **144**, 323 (1955).

[3] F. NELSON, *J. Amer. Chem. Soc.* **77**, 813 (1955).

[4] T. SCHOENFELD, M. WALD and M. BRUND, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 28, p. 48. United Nations (1959).

[5] K. A. KRAUS and G. E. MOORE, *J. Amer. Chem. Soc.* **75**, 1457 (1953).

was devised which appeared to be more reliable under these circumstances than the band-velocity column method described above. Weighed amounts of resin (ca. 50 mg) were placed into small columns to give shallow beds, ca. 3 mm high. Solutions of ^{7}Be in EDTA–NH_4Cl solutions of required pH were intermittently passed through the columns. The columns were centrifuged to remove most of the interstitial solution and counted to determine uptake of Be(II). Equilibrium was assumed established if on further passage of solution the counting-rate of the column was invariant; this sometimes required several days, particularly in the experiments carried out at low pH. Distribution coefficients D were computed from the counting rate of the solutions, the equilibrium counting-rate of the centrifuged columns and from the resin weights, after making corrections for the small amount of liquid adhering to the beads.

3. *Separations.* Separations were carried out with small resin columns, ca. 0·25 $cm^2 \times 4$ cm. Flow rates were between 0·5 and 1 cm/min. Metal concentrations were in the "tracer" range, usually less than 10^{-4} M.

4. *Tracers and solutions.* Most analyses were carried out radiometrically, using γ-counting with a well-type scintillation counter when possible. Samples containing "pure" β-emitters (^{45}Ca, ^{63}Ni) were flamed and counted on stainless steel disks in a β-proportional counter. The α-emitter ^{226}Ra was counted on flamed S.S. disks in an α-proportional counter.

The following tracers were used: $^{42}K(T_{\frac{1}{2}} = 12{\cdot}4$ hr); $^{7}Be(T_{\frac{1}{2}} = 53$ days); $^{46}Ca(T_{\frac{1}{2}} = 160$ days); $^{85}Sr(T_{\frac{1}{2}} = 54$ days); $^{133}Ba(T_{\frac{1}{2}} = 8$ years); $^{226}Ra(T_{\frac{1}{2}} = 1620$ years); $^{46}Sc(T_{\frac{1}{2}} = 85$ days); $^{48}V(T_{\frac{1}{2}} = 16{\cdot}2$ days); $^{51}Cr(T_{\frac{1}{2}} = 27$ days); $^{54}Mn(T_{\frac{1}{2}} = 300$ days); $^{60}Co(T_{\frac{1}{2}} = 5{\cdot}2$ years); $^{63}Ni(T_{\frac{1}{2}} = 80$ years); $^{65}Zn(T_{\frac{1}{2}} = 245$ days). The tracers, with the exception of ^{7}Be and ^{48}V, were obtained from the Radioisotopes Division of the Oak Ridge National Laboratory in a high state of purity as determined by their analyses.

Vanadium-48 and ^{7}Be tracers were prepared by cyclotron (proton) bombardment* of TiO_2 and LiF targets. The tracer ^{48}V was purified by cation exchange in HCl–HF and ^{7}Be by anion exchange in HCl–HF, methods which were described earlier.[10a] The eluates containing ^{48}V or ^{7}Be were evaporated to dryness in glass containers to remove excess HCl and to destroy HF, after which the residues were taken up with 0·01 M Na_2H_2Y solution.

EDTA–NH_4Cl solutions were prepared by adding aliquots of stock solutions of the di-hydrogen salts (Na_2H_2Y or $(NH_4)_2H_2Y$) to NH_4Cl solutions. Hydrochloric acid or ammonia solutions were added to adjust the pH to the desired value. To avoid complications from possible adsorption of Na^+ from EDTA solutions,[16] solutions of the ammonium salt ($(NH_4)_2H_2Y$), rather than on the more readily available sodium salt (Na_2H_2Y), were used at high pH.

Formation of EDTA complexes is reasonably rapid for the elements studied except Cr(III) for which the rate of formation is slow at room temperature but rapid at high temperature.[9] Hence, all EDTA stock solutions containing Cr(III) were heated a few minutes at ca. 95°C before use.

RESULTS AND DISCUSSION

1. *Adsorption of* EDTA. Possible adsorption of EDTA or its ions by anion exchangers might be expected to introduce serious problems in its utilization for separations. If adsorption were extensive, control of pH and EDTA concentration in the solutions would be difficult and prolonged pretreatment of the columns might become necessary.

In an attempt to determine quantitatively the extent of EDTA adsorption, a series of batch equilibrations was carried out using the chloride form of the resin and Na_2H_2Y–NH_4Cl solutions of pH 4·6. At this pH, the predominant EDTA species in solution is H_2Y^{2-} as indicated from the dissociation constants of H_4Y.†

Measurements of pH with a glass–calomel electrode assembly showed little change in acidity during the equilibration, suggesting that H_2Y^{2-} is entering the resin phase.

* We are indebted to the Oak Ridge National Laboratory Cyclotron Group for the bombardments.

† For computations, the following pk values for the successive dissociation constants of H_4Y at $\mu = 0{\cdot}1$, 25°C, were assumed: $pk_1 = 2{\cdot}20$, $pk_2 = 2{\cdot}74$, $pk_3 = 6{\cdot}21$, $pk_4 = 9{\cdot}96$. They were obtained by interpolation ($1/T$ vs. pk plots) of pk values at 20° and 30°C reported in Ref. 3.

[9] G. SCHWARTZENBACH and W. BIEDERMANN, *Helv. Chim. Acta* **31**, 459 (1948).

Vol. 15 1960

This conclusion was confirmed by chloride and EDTA analyses* before and after equilibration. According to the analyses, approximately two moles of chloride ions were released by the resin for each mole of EDTA adsorbed near pH 4·6 in accordance with the equation

$$2Cl^-_{(r)} + H_2Y^{2-} \rightleftharpoons H_2Y^{2-}_{(r)} + 2Cl^- \quad (1)$$

for which the expression

$$\frac{K_{H_2Y}}{G_{H_2Y}} = \frac{m_{H_2Y_{(r)}}}{m_{H_2Y}} \frac{m^2_{Cl}}{m^2_{Cl_{(r)}}} = K^m_{H_2Y} \quad (2)$$

may be written. Here K_{H_2Y} is the equilibrium constant which with proper choice of

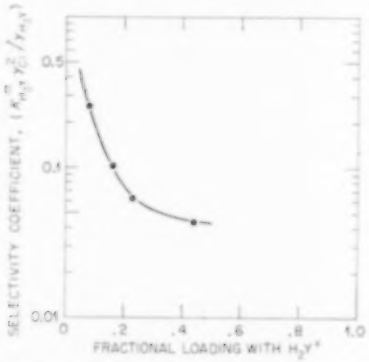

FIG. 1.—Selectivity as a function of loading for Cl^-–H_2Y^{-2} exchange.

standard states may be set equal to unity, G_{H_2Y} is the appropriate activity coefficient ratio for the ion exchange equilibrium, subscript (r) designates the resin phase and m is concentration in moles per kilogram resin or moles per litre of solution.

From the analytical data, the concentration quotient $K^m_{H_2Y}$ was computed. Since the experiments were carried out under conditions of varying ionic strength (initial m_{Cl}: 0·01 to 0·25; initial m_{H_2Y}: 0·01), the values of $K^m_{H_2Y}$ are not strictly comparable and a correction was made for the variation of the activity coefficients in the aqueous phase using the Debye–Hückel equation in the form $\log \gamma_i = -0{\cdot}509 z_i^2 \mu^{1/2}/(1 + 1{\cdot}5\mu^{1/2})$ for computation. The resulting values of $K^m_{H_2Y}\gamma^2_{Cl}/\gamma_{H_2Y}$ are summarized in Fig. 1. The selectivity of the resin for H_2Y^{2-} is quite small (selectivity coefficient less than unity) and rapidly decreases with loading. Thus at moderate ionic strength and low EDTA concentration, adsorption of H_2Y^{2-} can be held to very low values.

Adsorption of EDTA near pH 9, where HY^{3-} and Y^{4-} become the predominant species in the aqueous phase, was studied semi-quantitatively with a column breakthrough technique. A small column of the chloride form of the resin was treated with a large excess of NH_4Cl–$(NH_4)_2H_2Y$ solutions adjusted with NH_3 to pH 9. The equilibrated columns were centrifuged and adsorbed EDTA eluted with 1 M KCl from which EDTA is negligibly adsorbed. The pH of the effluent and the amount of

* EDTA was determined by acid base-titration (NaOH) of hydrogen ions liberated on addition of excess $CaCl_2$ to the solutions. See: G. SCHWARTZENBACH, W. BIEDERMAN and F. BANGERTER, *Helv. Chim. Acta* **29**, 811 (1946).

acid liberated by addition of excess $CaCl_2$ were determined. In a 0·1 M NH_4Cl–10^{-3} M $(NH_4)_2H_2Y$ solution (pH 9) the resin was found to remain essentially in the chloride form with only 5% of the exchangeable chloride ions displaced by EDTA species.

2. *Adsorption of metal–EDTA complexes.* In view of the high stability of EDTA complexes, most metals, even at low (free) EDTA concentrations, are essentially completely converted to complex species. For di- and trivalent ions, particularly at trace concentrations, this implies essentially quantitative conversion to negatively charged complexes. The variation of adsorbability of these complexes with supporting electrolyte concentration should follow the relationship

$$\frac{d(\log D_B)}{d(\log m_A)} = -\frac{b}{a} + \frac{b}{a}\frac{d(\log m_{A_{(r)}})}{d(\log m_A)} - \frac{1}{a}\frac{d(\log G_{AB})}{d(\log m_A)} \qquad (3)$$

which is typical for "stable" complexes and which was discussed recently in considerable detail.[10] In equation (3), D_B is the distribution coefficient of the anion B^{-b}, m_A is the concentration of the eluting anion A^{-a} and G_{AB} is the appropriate activity coefficient ratio for the ion exchange equilibrium ($G_{AB} = g_{B^a{}_{(r)}} g_A{}^b / g_B{}^a g_{A^b{}_{(r)}}$).

According to equation (3), b/a, the ratio of the charges of adsorbed vs. eluting ion may be determined readily from the slope of a log D_B vs. log m_A plot if $d(\log m_{A_{(r)}})/d(\log m_A)$ and $d(\log G_{AB})/d(\log m_A)$ are small. The term $d(\log m_{A_{(r)}})/d(\log m_A)$ is usually negligibly small if B^{-b} is at trace concentration, the supporting electrolyte concentration is low and the resin of reasonably high cross-linkage. In order to keep $d(\log G_{AB})/d(\log m_A)$ small, both the activity coefficient ratio for the resin ($g_{B^a{}_{(r)}}/g_{A^b{}_{(r)}}$) and the ratio for the aqueous phase ($g_A{}^b/g_B{}^a$) should vary little. The activity coefficient ratio for the resin can be considered constant if the concentration of B in the resin is small (tracer experiments) and there is no change in resin invasion. The activity coefficient derivative for the aqueous phase, however, is negligible only at very low ionic strength or when $a = b$ and the activity coefficients follow the Debye–Hückel equation. All the experiments to be described were carried out at trace-metal concentration and low ionic strength, hence these simplifications should apply and the slopes of log–log plots of D_B vs. m_A should closely approximate the charge ratio $-b/a$.

In the adsorption of EDTA complexes, under conditions where they are essentially completely formed, one can visualize two types of experiments: (1) experiments as a function of ligand concentration in the absence of other supporting electrolytes; (2) experiments at constant ligand concentration as a function of concentration of a non-complexing supporting electrolyte. To check the validity of the various relationships, both types of experiments were carried out with a few EDTA complexes of known charge.

Adsorption of Cr(III) and V(IV) from Na_2H_2Y solutions (pH 4·6) was studied using the resin essentially in the H_2Y^{2-} form. The results are given in Fig. 2 as log–log plots of D_V vs. m_{H_2Y}. The slopes $d(\log D_V)/d(\log m_{H_2Y})$ are approximately $-\frac{1}{2}$ and -1 for Cr(III) and V(IV) respectively. Since the eluting ion is presumably H_2Y^{2-}, $a = -2$, and one concludes from the observed slopes that the charge of the Cr(III) complex is -1 and that of the V(IV) complex is -2. These charges are consistent with the species proposed, CrY^{-}[9] and VOY^{2-}[11].

[10] K. A. KRAUS and F. NELSON, *The Structure of Electrolytic Solutions* (Edited by W. J. HAMER), Chapter 23, p. 340. John Wiley, New York (1959).
[11] G. SCHWARZENBACH and J. SANDERA, *Helv. Chim. Acta* **36**, 1089 (1953).

Vol. 15 1960

Measurements of adsorbabilities at constant EDTA concentration and variable supporting electrolyte concentration are complicated by possible adsorption of EDTA by the resin which might become increasingly serious as the supporting electrolyte concentration decreases. Since, as discussed in the first part of this paper, the selectivity of the resin for EDTA is moderately small, this problem can be partially circumvented by operating at low EDTA concentration and moderately high ionic strength.

Adsorbabilities of Mn(II), Co(II), Ni(II), Zn(II), Sc(III), and V(IV) were

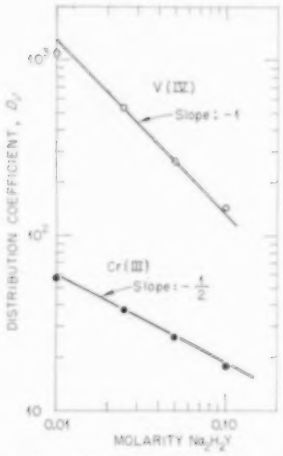

FIG. 2.—Adsorption of V(IV) and Cr(III) from EDTA solutions, pH 4·6.

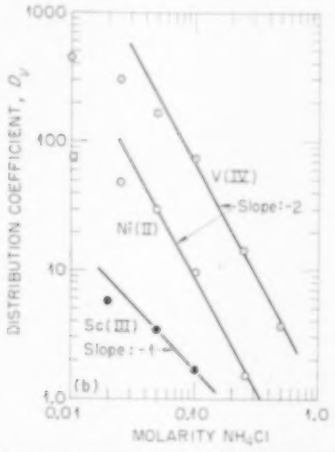

FIG. 3.—Adsorbability of Ni(II), Sc(III) and V(IV) from 0·01 M EDTA–NH_4Cl solutions, pH 4·6.

determined in NH_4Cl solutions containing 0·01 M Na_2H_2Y (pH 4·6). The results for Ni(II), Sc(III) and V(IV) are summarized in Fig. 3; those for Mn(II), Co(II), and Zn(II) are not shown since they were similar to those of Ni(II). The slopes $d(\log D)/d(\log m_{NH_4Cl})$ were approximately −2 for Mn(II), Ni(II), Co(II), Zn(II) and V(IV) at the higher NH_4Cl concentrations and approximately −1 for Sc(III). These are the slopes to be expected if the species are MnY^{2-}, CoY^{2-}, NiY^{2-}, ZnY^{2-}, VOY^{2-} and ScY^{-}, the formulae usually suggested for the complexes in EDTA solutions.[3] The observed data seriously deviate from the expected slopes at low m_{NH_4Cl} presumably because under these conditions substantial absorption of H_2Y^{2-} by the resin occurs, changing the composition of the resin and hence making the assumption of invariance of activity coefficients in the resin phase inapplicable.

In the case of EDTA complexes of Cr(III), it has been proposed[9] that the species CrY^{-} exists near pH 4·6 and the species $CrOHY^{2-}$ at high pH. The charges of these species were readily verified through measurement of distribution coefficients of Cr(III) from NH_4Cl–0·01 M EDTA solutions adjusted to pH 4·6 and pH 9. The results of the measurements are given in Fig. 4, a plot of $\log D_V$ vs. $\log m_{Cl}$. Near pH 9 the slope is ca. −2 and near pH 4·6 it is ca. −1, as expected.

3. *Adsorbabilities as a function of pH.* Most of the experiments described in the previous section were carried out under conditions where the fraction F_{MY} of the metal M^{r+} converted to the adsorbable complex MY^{r-4} is essentially unity. At substantially lower free Y^{4-} concentrations, conditions may be found where F_{MY}

becomes less than unity and where adsorbability might thus decrease in proportion to F_{MY}. Presumably, this will occur at sufficiently high acidity and hence studies were carried out on adsorbabilities of various metals as a function of pH at constant EDTA and supporting electrolyte concentrations.

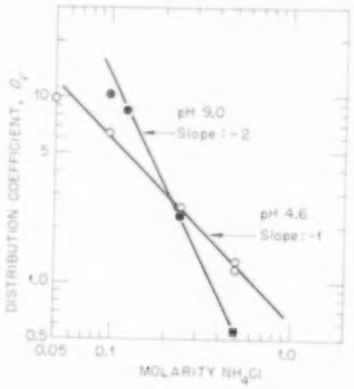

FIG. 4.—Adsorption of Cr(III) from 0·01 M EDTA–NH_4Cl solutions.

The results for a number of divalent elements are summarized in Fig. 5 as log–log plots of D_v vs. m_H. The measurements were carried out at trace metal concentration, $7{\cdot}5 \times 10^{-4}$ M EDTA, and 0·1 M Cl^-(NH_4Cl–HCl). The distribution coefficients

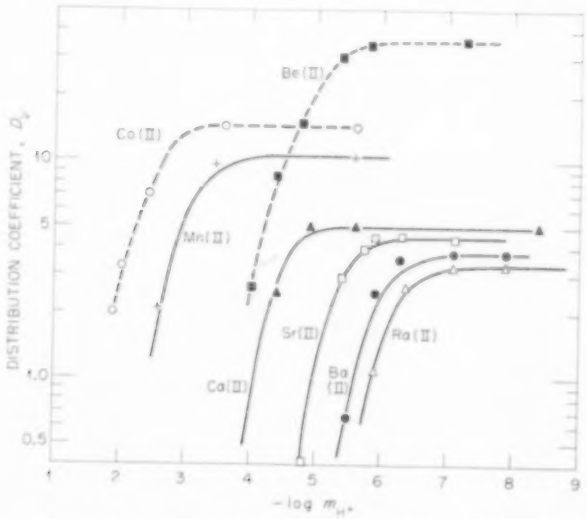

FIG. 5.—Adsorption of several elements as a function of acidity. (0·1 M chloride, $7{\cdot}5 \times 10^{-4}$ M EDTA). (—— Computed curves).

reach asymptotes at low acidity. The value of D_v in the asymptote (defined as D_v^*) reflects the intrinsic adsorbabilities or selectivity coefficients $K^{(r)}$ defined as

$$K^{(r)}_{MY} = \frac{(MY^{r-4})_{(r)}(Cl^-)^{4-r}}{(MY^{r-4})(Cl^-)^{4-r}_{(r)}} = \frac{K_{MY}}{G_{MY}} \qquad (4)$$

Vol. 15 1960

where ( ) indicate concentrations of species; K_{MY} is the constant for the ion exchange equilibrium (unity with proper choice of standard states) and $G_{MY} = (g_{MY(r)}g_{Cl}^{4-r})/(g_{MY}g_{Cl(r)}^{4-r})$ the appropriate activity coefficient quotient.

The computed values of $K_{MY}^{(r)}$ (concentration expressed as moles/kg dry resin and moles/liter soln) are summarized in Table 1. The selectivity coefficients for most of the

TABLE 1.—SELECTIVITY COEFFICIENTS OF A NUMBER OF DIVALENT METAL–EDTA COMPLEXES (DOWEX-1 × 4, CHLORIDE FORM)

Element	$K_{MY}^{(r)}$	Element	$K_{MY}^{(r)}$
Be(II)	0·104	Ra(II)	0·010
Ca(II)	0·014	Mn(II)	0·031
Sr(II)	0·013	Co(II)	0·042
Ba(II)	0·011		

alkaline earths (Ca^{2+}–Ra^{2+}) are remarkably similar and decrease in regular order from Ca to Ra. The selectivity coefficient for Be(II), however, is almost an order of magnitude larger than those of the other alkaline earths; those for the transition elements Mn(II) and Co(II) lie intermediate.

The characteristic rapid decreases in adsorbabilities at higher acidities presumably reflect the instabilities of the complexes. If we assume tentatively that only the species MY^{2-} is significantly adsorbed by the resin and that this species predominates in the pH range where D_v is independent of acidity, we may compute the fraction F_{MY} by the relationship $F_{MY} = D_v/D_v^*$. From the values of F_{MY}, one may compute the stability constants of the complexes provided the concentration of Y^{4-} is known. Conversely, if the constants for the equilibria in the aqueous phase are established, one may compute F_{MY} as a function of acidity and obtain "predicted" values of $D_v = D_v^* F_{MY}$ for comparison with the observed values. For the divalent ions, the principal species are M^{2+}, MY^{2-} with the conjugate acid HMY^- occasionally being of importance (see e.g. Reference 3). With these restrictions and the definitions

$$k_{10}^{(r)} = \frac{(M^{2+})(Y^{4-})}{(MY^{-})} = k_{10}/G_{10} \tag{5}$$

and

$$k_a^{(r)} = \frac{(H^+)(MY^{2-})}{(HMY^-)} = k_a/G_a \tag{6}$$

one may compute F_{MY} from the relationship

$$\frac{1}{F_{MY}} - 1 = k_{10}^{(r)}/(Y^{4-}) + (1/k_a^{(r)})(H^+) \tag{7}$$

In these equations, k refers to stability constants, $k^{(r)}$ to concentration quotients, G to activity coefficient quotients and parentheses to concentration of species.

In the computation of the "theoretical" curves, shown as solid lines in Fig. 5, the following $pk_a^{(r)}$ values were used: Be: $pk_{10}^{(r)} = 9{\cdot}3$; Ca: $pk_{10}^{(r)} = 10{\cdot}57$, $pk_a^{(r)} = 3{\cdot}07$; Sr: $pk_{10}^{(r)} = 8{\cdot}63$, $pk_a^{(r)} = 3{\cdot}93$; Ba: $pk_{10}^{(r)} = 7{\cdot}76$, $pk_a^{(r)} = 4{\cdot}57$; Mn: $pk_{10}^{(r)} = 14{\cdot}04$,

$pk_a^{(1)} = 3{\cdot}12$; Co: $pk_{10}^{(1)} = 15{\cdot}76$, $pk_a^{(1)} = 3{\cdot}10$. These values, except $pk_{10}^{(1)}$ for Be(II), were obtained or calculated from the data given in Ref. 3. They generally refer to 20°C. The $pk_{10}^{(1)}$ values for Ca(II) and Co(II) refer to 25°C; they were obtained by interpolation of the data given in the tables. The value of $pk_{10}^{(1)}$ for Be(II) was obtained from recent cation exchange experiments in 0·1 *M* NH_4Cl[12] and refers to 25°C.

The agreement between observed and calculated adsorption functions appears satisfactory for Ca(II), Sr(II), Ba(II) and Mn(II). In the case of Co(II), the computed curve (not shown) lies substantially below the observed points; for example at $(H^+) = 10^{-3}$ the computed distribution coefficient is ca. 5 while the observed distribution coefficient is near fourteen. In this case, the fraction of the element in the form of the acid complex HMY^- is large ($F_{HMY} = 0{\cdot}67$) and the adsorbability of this complex apparently cannot be ignored.

The calculated adsorption function for Be(II) (not shown) also lies substantially below the observed points. The discrepancy also might be due to adsorption of acid complexes such as $HBeY^-$. But in this case the discrepancy might also result from more profound reasons since the rate of equilibration for this element was very much slower than for the other divalent elements studied.

Since stability constants for Ra(II) are not available, the distribution function was used to calculate $k_{10}^{(1)}$ using $pk_{10}^{(1)} = 7{\cdot}4$ the solid curve shown in Fig. 5 was obtained.

4. *Separations.* A number of separations may be devised on the basis of the data presented. In general, these separations may be classified as (1) those based on differences in selectivity of the resin for the complexes; (2) those based on differences in charge of the complexes which permits separations by control of ionic strength; and (3) those based on the fraction of the metal complexed—either through control of acidity or control of EDTA concentration.

For most elements of the same charge type, the differences in selectivity are not sufficiently large to permit separations with small columns. A particularly favourable case is illustrated in Fig. 6, separation of Ni(II) from V(IV) under conditions where Ni(II) presumably exists as NiY^{2-} and V(IV) as VOY^{2-}. For this separation, 0·02 ml of 0·01 M EDTA solution (pH 4·6) containing tracers of these elements as well as of potassium (added as a typical "non-adsorbable" element) was added to a small column of the resin in the chloride form, pretreated with 0·10 M NH_4Cl–0·01 M EDTA. Potassium was removed with less than one column volume of 0·01 M EDTA; Ni(II) was removed with 0·01 M EDTA–0·40 M NH_4Cl and finally V(IV) with 2·0 M NH_4Cl–0·01 M EDTA.

Since in many cases the more strongly adsorbed complex is also the more stable one, it becomes feasible to augment intrinsic separabilities by proper pH control. Indeed, separations based on pH control are probably in general the most powerful ones. A typical example is illustrated in Fig. 7. For this separation, a small aliquot of a solution containing tracers of Mn(II) and Co(II) in 0·09 M NH_4Cl–0·01 M HCl and $7{\cdot}5 \times 10^{-4}$ M EDTA was added to a small column of resin pretreated with the same supporting electrolyte. On elution with the same electrolyte, Mn(II) appeared in the effluent at approximately 0·8 column volumes. On continued elution, Co(II) appeared in a rather broad band, but well separated from Mn(II), with peak maximum near 3·7 column volumes.

The technique of effecting separations by control of the fraction of the metal

[12] F. NELSON Unpublished results.

Vol. 15 1960

complexed is, of course, also the basis of cation exchange separations with EDTA and other complexing agents, where the element forming the most stable complex is eluted first. In the anion exchange method, the more weakly complexed element is eluted

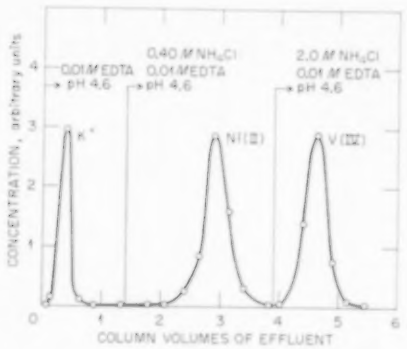

FIG. 6.—Separation of K^+, Ni(II) and V(IV) with EDTA solutions.

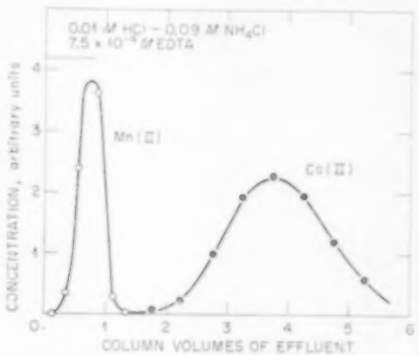

FIG. 7.—Separation of Mn(II) and Co(II) in EDTA solutions.

first. By combining the two techniques, elution order, which is often of considerable importance in separations, may be controlled.

Separations involving Cr(III) are often difficult because of the slow rate of

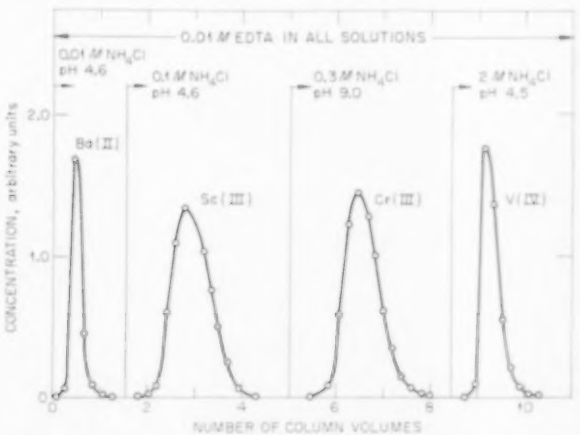

FIG. 8.—Separation of some elements in EDTA solutions.

formation of the EDTA complex. On heating Cr(III) in EDTA solutions, an adsorbable Cr(III) complex is formed which is readily handled in anion exchange separations. This complex (CrY^-) seems to be in rapid equilibrium with a hydrolysed species ($CrOHY^{2-}$) of a different charge. This equilibrium may be exploited for separations as illustrated in Fig. 8. A mixture of Ba(II), Sc(III), Cr(III) and V(IV) in 0·01 M EDTA–0·01 M NH_4Cl (pH 4·6) was added to a small resin column. On elution with the same supporting electrolyte, Ba(II) appears immediately in the effluent since at this pH and EDTA concentration it is essentially uncomplexed.

Scandium(III) was eluted with 0·1 M NH_4Cl–0·01 M EDTA solution. To remove chromium with a minimum of eluent, elution was continued with 0·3 M NH_4Cl–0·01 M EDTA at pH 9·0. Vanadium(IV) was removed with 2·0 M NH_4Cl.

These and earlier data clearly demonstrate that excellent separations may be achieved in EDTA solutions. However, the generally low selectivity of the resin for the metal–EDTA complexes places severe restrictions on the useful ionic strength range in which these separations can be carried out.

Vol.
15
1960

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SEPARATION OF *TRANS*-CURIUM ELEMENTS FROM LARGE QUANTITIES OF CURIUM, BY LIQUID–LIQUID EXTRACTION*

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(*Received* 5 *November* 1959)

Abstract—A solvent extraction procedure, using 100 per cent normal tributyl phosphate and 12 M HCl for the separation of *trans*-curium elements from large quantities of curium, is described. The method, tested on pure curium and californium, was then applied successfully to the separation of curium and californium from material resulting from the reprocessing of an irradiated plutonium sample. The following results were obtained for the reprocessing: (92 ± 11) per cent of the californium was recovered containing (0·74 ± 0·05) per cent of the original curium and (100 ± 7) per cent of the curium was recovered containing an undetectable amount of the original californium.

IN order to separate and identify by the ion-exchange technique the actinide elements of atomic number 97 and higher, resulting from a long-term neutron irradiation of Pu, it was first necessary to eliminate the bulk of the curium contained in the sample as ^{244}Cm and ^{242}Cm. Both of these isotopes have a very high specific activity due to their relatively short half-lives and their presence reduces the efficiency of subsequent ion exchange separations of *trans*-curium elements. Not only is the resin partially decomposed by this activity, but the radiation decomposition of the solutions generates gases that disturb the resin bed and greatly decreases the efficiency of the column operation. Liquid–liquid extraction is not affected by these inconveniences, and this method was successfully used for removing the bulk of the curium before separation of the higher actinides.

1. *Chemical system*

The chemical system applied to this extraction was identical to the one described by PEPPARD *et al.*[1] and by GRAY and THOMPSON.[2] In this system, the actinides in a 12 M hydrochloric acid solution are extracted by 100 per cent n-tributyl phosphate (TBP). Under these conditions and after thorough scrubbing of the organic phase with 12 M HCl, the californium will concentrate in the TBP, whereas the curium will accumulate in the aqueous phase. The distribution coefficients for curium and californium** (defined as the ratio of the concentration of the element in the organic phase to the concentration of the element in the aqueous phase at equilibrium) were for the system used here:

$$K_{Cm} = 0{\cdot}073$$

$$K_{Cf} = 0{\cdot}913$$

The separation factor $\left(\text{distribution coefficient ratio } \frac{K_{Cf}}{K_{Cm}}\right)$ was therefore equal to 12·4.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
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§ Physics Department, University of Illinois, Urbana, Illinois.
** From this point on, the text will use the symbols for curium and californium, Cm and Cf respectively.

[1] D. F. PEPPARD, J. P. FARIS, P. R. GRAY and G. W. MASON, *J. Phys. Chem.* **57**, 294 (1953).
[2] P. R. GRAY and S. G. THOMPSON, Report UCRL-2069 (1952).

Preliminary results have shown that the distribution coefficients of einsteinium and fermium are in excess of the californium.[3]

2. *Flow sheet*

A multiple-extraction scheme with scrubbing, i.e. a "batch" crosscurrent method, was used rather than a countercurrent technique. The principal reasons for this choice were the following:

(1) The process is more versatile, permitting easy control at any stage and is thus a better tool for laboratory research.

(2) It permits the handling of small volumes of radioactive solutions and requires a minimum number of theoretical stages.

The requirements for our separation of Cm and Cf were the following:

(a) less than 1 per cent of Cm in the Cf product.

(b) the highest possible recovery of the Cf.

Using an organic-to-aqueous ratio of two, a variety of separation schemes were examined theoretically using procedures described by Alders[4].

The flow sheet which satisfied the separation requirements and had a minimum number for theoretical stages is shown in Fig. 1. In this flow sheet the following three symbol code has been used to

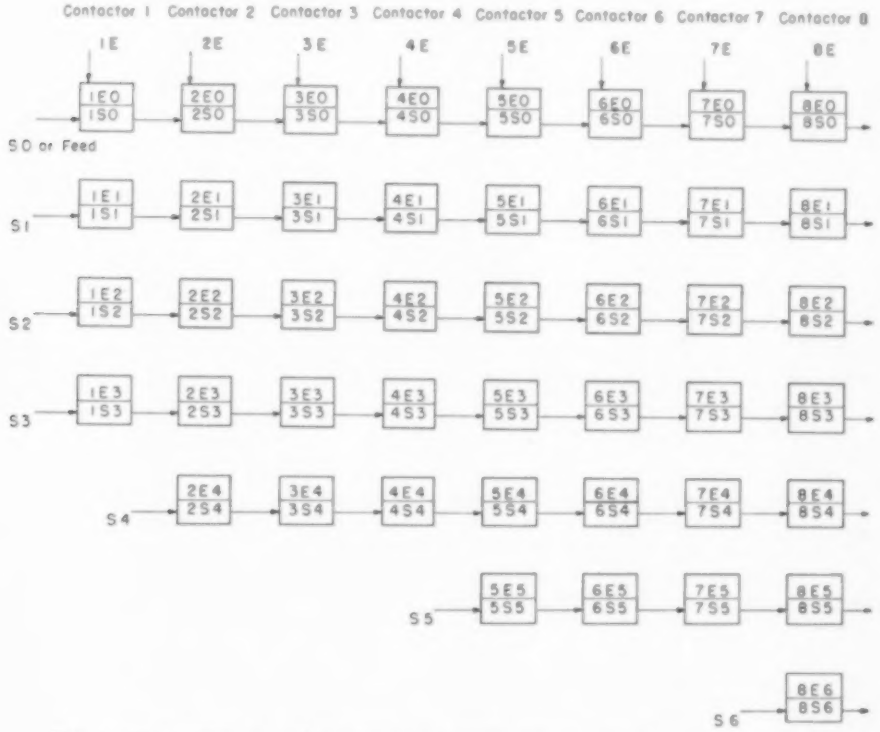

Fig. 1.—The multiple extraction scheme (with scrubbing) used for the separation of Cm and Cf.

designate any phase: the first number refers to the contactor in which the contact occurred; the second symbol, a letter, indicates whether it is an extractive (*E*) or scrub (*S*) phase; finally, the second number, characterizes which scrub solution has been used, the original feed being referred to as scrub *O* (*SO*).

[3] D. F. Peppard and G. W. Mason. Private communication (1959).

[4] L. Alders, *Liquid–Liquid Extraction*. Elsevier, Amsterdam (1955).

Vol. 15 1960

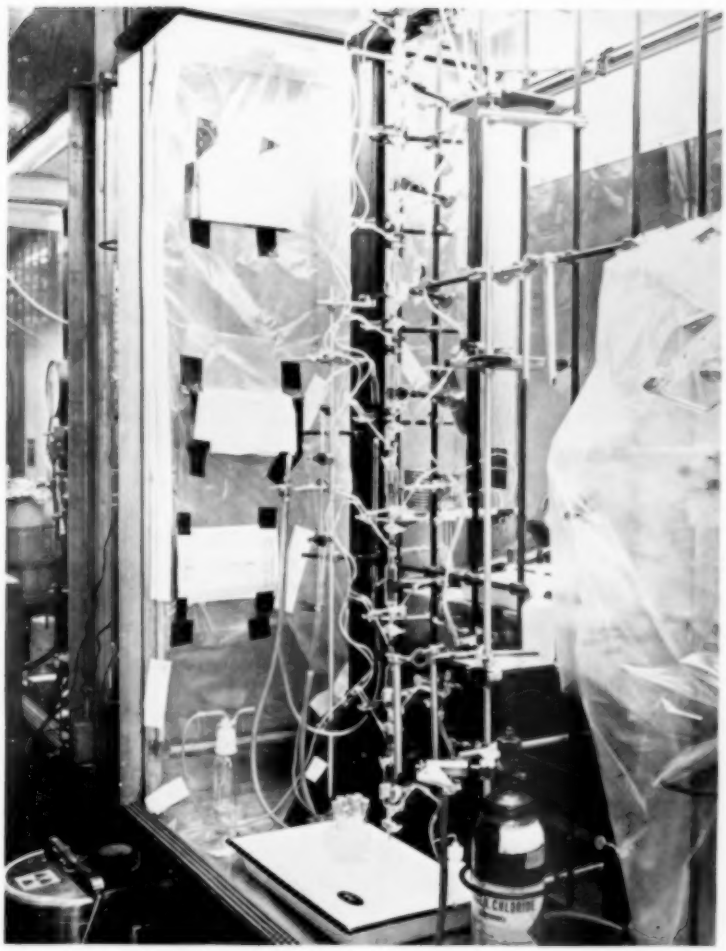

FIG. 2.—View of the apparatus in a vacuum frame hood consisting of eight contactors connected in a vertical series.

Vol.
15
1960

The operations were the following: The eight contactors were filled with the eight organic phases (1*E* to 8*E*). These organic phases will remain in their respective contactors during the whole operation. The aqueous feed *SO* was then introduced into contactor 1, contacted with the organic phase 1*EO* and after settling, transferred to contactor 2 where the same procedure was repeated before the aqueous phase 2*SO* was transferred to contactor 3 and so on.

After the organic phase has been contacted with the aqueous feed solution, the first scrub (*S*1) was introduced into contactor 1 and treated in the same way as the aqueous feed solution.

The calculations showed that after the organic phase in the first contactor had been scrubbed three times, it satisfied the separation requirements. Thus the fourth scrub began in contactor 2. Then the organic phases 2*E*4, 3*E*4, and 4*E*4 were satisfactory and the fifth scrub began in contactor 5 and so on. The percentages of Cm and Cf in the aqueous and organic phases calculated on this basis are given in Table 1.

TABLE 1.—CALCULATED PERCENTAGE OF Cm AND Cf*

		Curium (%)	Californium (%)
Aqueous	8*S*0	33·43	0·02
	8*S*1	34·23	0·13
	8*S*2	19·72	0·37
	8*S*3	8·41	0·80
	8*S*4	2·95	1·41
	8*S*5	0·84	2·03
	8*S*6	0·11	1·31
		99·69	6·07
Organic	1*E*3	0·027	17·43
	2*E*4	0·012	15·94
	3*E*4	0·037	19·74
	4*E*4	0·077	16·97
	5*E*5	0·018	7·87
	6*E*5	0·043	7·83
	7*E*5	0·078	5·76
	8*E*6	0·016	2·39
		0·31	93·93

* $K_{Cm} = 0{\cdot}073$, $K_{Cf} = 0{\cdot}913$, volume organic/volume aqueous = 2.

3. *Description of the contactors*

The high α-activity of the feed material required the separation equipment to be designed such that it was a closed system and could be operated in a glove-box. The apparatus, as built, consisted of eight units connected in a vertical series as shown in Fig. 2. Each unit, about 120 mm in length, consisted of Pyrex tube 30 mm in diameter narrowing at both ends to a 10 mm diameter, with a balljoint at the top and a stopcock at the bottom (see Fig. 3).

Slightly above this stopcock, in the small diameter section, there was a fritted glass filter of medium porosity. Its purpose was to allow the passage of the mixture of gas which will assure the mixing of the two phases and facilitated their separation by allowing the aqueous phase to go through while holding the organic phase. (It was necessary to check the porosity of the filter after it was sealed in the tube because its porosity is affected by the temperatures encountered in making the seals.)

The two phases were mixed by bubbling an air-anhydrous HCl mixture. A volume ratio of air/HCl = 3 was found to be satisfactory in maintaining the acidity constant in all units during a run. The inlet flow of the gas mixture was controlled by a microstopcock and the volume ratio of the gases by flow meters. The gas entered the unit through a 5 mm diameter tube in a small section between the stopcock of the unit and the fritted glass filter (see Fig. 3). An exit for the gas mixture was provided

via a three-way stopcock in the short section of tubing which served to join two units. This stopcock also allowed a slight pressure to be applied on the liquids in order to force them through the fritted glass.

All the gas inlets were joined in a common line and a reasonably constant gas pressure was achieved by the use of a bleeder valve at the top of the apparatus. Likewise all outlets were joined to one line which went to a gas scrubber which removed the air-borne activity. A small side tube, also provided with a stopcock, (V), allowed the inlet of the feed and the scrub solutions in contactors 1, 2, 5 and 8.

One cycle of operation of the unit in Fig. 3 will illustrate the use of the stopcocks: Let us assume that the two phases are in the contactor *A*. The stopcock (I) is closed and the two phases do not flow

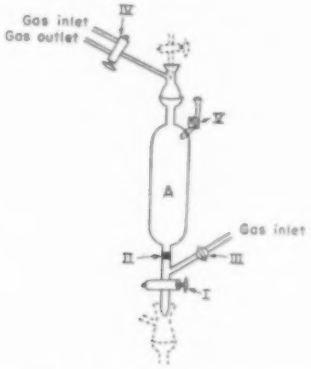

FIG. 3.—Diagrammatic sketch of one contactor.

through the fritted glass filter (II) because of a slight pressure applied through the microstopcock (III). The three-way stopcock (IV) is set so that the gas can escape. The microstopcock (III) is now opened further to permit gas to enter and mix the phases. After mixing, the microstopcock (III) is closed and the two liquids allowed to settle. (I) is then opened and the heavy aqueous phase allowed to run into the next contactor, [this could be accelerated by applying a slight pressure through (IV)]. When the light phase touches the fritted glass filter, (I) is closed and (III) is opened slightly to prevent the flow of the organic solution. (V) allowed the inlet of fresh scrub solution. The entire assembly was set up in a vacuum frame-hood with glove panels. In the case of highly radioactive solutions, manipulations were made (using the gloves) with specially designed rods to avoid prolonged close contact. Furthermore, to facilitate experimentation and to minimize the spread of activity, provisions were made so that samples could be taken, aliquots made, and plates prepared for counting within the vacuum frame hood.

Vol. 15 1960

4. *Experimental data and results*

(a) *Synthetic solution of* Cm *and* Cf. Several runs were done with synthetic solutions of Cm and Cf, i.e. solutions prepared from highly purified Cm and Cf. The results for one of them will be given below:

The feed solution was a mixture of Cm and Cf chlorides in 12 M HCl. The volume of the feed was 2 ml. The organic solution was a 100 per cent n-tributyl phosphate pre-equilibrated with 12 M HCl. The scrub solution was a "barren" 12 M HCl solution.

In each contact, the ratio of organic to aqueous was equal to two. The mixing and the settling times were about 3 min each. At the end of the run, a sample from each phase was taken and plated on platinum disks for alpha and fission counting. The amount of Cm and Cf present in a solution were determined from measurements of

alpha and fission counting-rates of the solution. By using the calculated ratios of the specific fission activity to the specific α-activity for Cm and Cf, namely $a_{Cm} = 2{\cdot}8 \times 10^{-6}$ and $a_{Cf} = 5{\cdot}4 \times 10^{-2}$, it follows that the total quantity of Cm, Q_{Cm} (expressed in α-counts per minute) and of Cf, Q_{Cf} (expressed in fission per minute) are given by:

$$Q_{Cm} = N_\alpha - a_{Cf}N_F$$
$$Q_{Cf} = N_F - a_{Cm}N_\alpha$$

Where N_α and N_F represent the total number of α-counts and total number of fission counts per minute respectively.

TABLE 2.—RESULTS OF THE RUN ON A SYNTHETIC SOLUTION OF Cm AND Cf

		Curium (%)	Californium (%)
Aqueous	8S0	23·5 ± 1·2	not detectable
	8S1	35·3 ± 1·8	not detectable
	8S2	17·8 ± 0·9	not detectable
	8S3	11·0 ± 0·5	not detectable
	8S4	5·8 ± 0·3	1·7 ± 1·4
	8S5	2·1 ± 0·1	2·3 ± 0·5
	8S6	0·34 ± 0·02	1·9 ± 0·1
		95·8 ± 2·4	5·9 ± 1·5
Organic	1E3	0·106 ± 0·005	10·3 ± 0·5
	2E4	0·033 ± 0·002	10·1 ± 0·5
	3E4	0·079 ± 0·004	21·0 ± 1·0
	4E4	0·134 ± 0·007	16·4 ± 0·8
	5E5	0·040 ± 0·002	11·5 ± 0·6
	6E5	0·093 ± 0·005	11·2 ± 0·6
	7E5	0·175 ± 0·009	7·2 ± 0·4
	8E6	0·046 ± 0·002	3·4 ± 0·2
		0·706 ± 0·014	91·1 ± 1·7
Additional recovery		1·23 ± 0·06	4·7 ± 0·4
Total recovery		97·7 ± 2·4	101·7 ± 2·3

The amount of Cm and Cf in the feed solution was obtained from the results of several-day counts of two aliquots.

Feed $\quad Q_{Cm} = 8{\cdot}6 \pm 0{\cdot}4 \times 10^{10}$ α-counts per minute

$\quad\quad Q_{Cf} = 1{\cdot}54 \pm 0{\cdot}38 \times 10^{5}$ fissions per minute.

The error reported is based upon the error made on sampling the solution (±5 per cent) and in the case of Cf, also on the uncertainty in the spontaneous fission half life of ^{244}Cm (±5 per cent).[5]

The results of the run, expressed in percentages of the feed recovered, are given in Table 2. These results should be compared with the calculated values given in

[5] A. GHIORSO, G. H. HIGGINS, A. E. LARSH, G. T. SEABORG and S. G. THOMPSON, *Phys. Rev.* **87**, 163 (1952).

Table 1. After the run, the apparatus was washed thoroughly and (1·23 ± 0·06) per cent of Cm and (4·7 ± 0·4) per cent of Cf recovered. The total recovery was

$$(97{\cdot}7 \pm 2{\cdot}4)\%\ \text{Cm and } (101{\cdot}7 \pm 2{\cdot}3)\%\ \text{Cf.}$$

Of this, (91·1 ± 1·7) per cent of the Cf was recovered as one combined organic fraction containing (0·706 ± 0·014) per cent of Cm and (95·8 ± 2·4) per cent of the Cm was recovered as one combined aqueous fraction containing (5·9 ± 1·5)% Cf.

The Cf fraction could be converted into an aqueous solution by stripping thoroughly the collected organic phases using a very dilute HCl solution.

(b) *Material from irradiated plutonium.* The method was then applied to a solution of heavy elements originating from the dissolution of a highly irradiated plutonium sample. After the dissolution of the sample and the separation of the fission products by ion exchange techniques, the 3 ml feed solution contained the following quantities:

Feed
$$Q_{Cm} = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{12}\ \alpha\text{-counts per minute}$$
$$Q_{Cf} = 1{\cdot}20 \pm 0{\cdot}13 \times 10^{7}\ \text{fissions per minute.}$$

The liquid–liquid extraction was carried on in the same way as for a synthetic solution. The whole experiment took 4 hr. Because of the radiation decomposition of the resin during the earlier ion exchange separation, some organic products were present in the feed solution. Their presence produced some emulsification during the contact with the first organic phase. As a result, the aqueous phase was not quantitatively transferred into the second contactor, however, the remainder was recovered with scrub 1.

Forty-eight millilitres of organic solution were recovered and assayed to give:

$$Q_{Cm} = 2{\cdot}0 \pm 0{\cdot}1 \times 10^{10}\ \alpha\text{-counts per minute}$$
$$Q_{Cf} = 1{\cdot}10 \pm 0{\cdot}05 \times 10^{7}\ \text{fissions per minute}$$

or (92 ± 11) per cent of the Cf and (0·74 ± 0·05) per cent of the Cm originally present. The combined aqueous solutions were assayed as

$$Q_{Cm} = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{12}\ \alpha\text{-counts per minute}$$
$$Q_{Cf} = 5 \pm 1 \times 10^{5}\ \text{fissions per minute}$$

or (100 ± 7) per cent of the Cm containing an undetectable amount of the original Cf.

CONCLUSION

This method proved to be very satisfactory to separate tracer quantities of Cf from milligram quantities of Cm. The preliminary results of Peppard and Mason for einsteinium and fermium show that the method should also be applicable to these elements. Although large amounts of Cm and Cf were present, no troubles were encountered due to the radiation decomposition of the solution. A slight emulsification appeared in the first contactor after mixing the feed and the first organic phase, but the emulsion could be separated by slightly increasing the volume of the aqueous

Vol. 15 1960

phase without affecting the final results. The apparatus could be built on a larger scale by small changes in the design of the contactors. The separation of these elements by a countercurrent technique is now under development.

Acknowledgements—One of the authors (N. M. I) would like to express her gratitude to Argonne National Laboratory and in particular to Dr. W. MANNING, director of the chemistry division, for the kind invitation to work at the laboratory.

We are grateful to the heavy element group at Argonne, for supplying the materials used in these studies. It is also a pleasure to acknowledge the helpful discussions with D. F. PEPPARD and G. W. MASON.

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SYNERGIC EFFECTS IN THE SOLVENT EXTRACTION OF THE ACTINIDES—I

URANIUM(VI)

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Abstract—By using ^{233}U the solvent extraction of uranium(VI) from nitric acid into mixtures of 1,1,1-trifluoro-3-2′-thenoylacetone (TTA) and tri-n-butyl phosphate (TBP) or tri-n-butyl phosphine oxide (TBPO) in cyclohexane has been studied. The extraction coefficient has been found to be greater for such mixtures than for either component alone, the maximum enhancement in extraction being of the order of 10^3 and 10^4 respectively.

The formulae of the extracted species have been shown to be UO_2X_2, TBP and UO_2X_2, 3TBPO (HX = TTA) and their mixed equilibrium constants calculated.

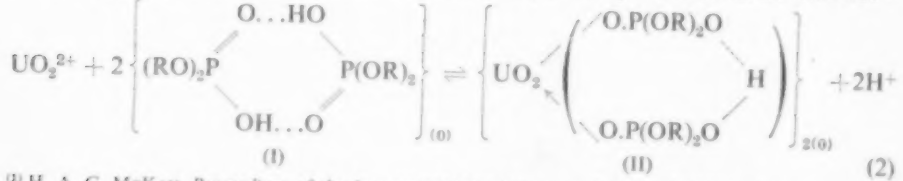
The general problem of synergism in the solvent extraction of metal complexes has been discussed.

WHEN tri-n-butyl phosphate (TBP) was first introduced as a reagent for the solvent extraction of certain metals from their solutions in nitric acid, discrepancies were often reported between values for extraction coefficients obtained in different laboratories using different samples of the phosphoric ester. The source of these discrepancies was soon traced to the use of inhomogenous material containing varying percentages of partly esterified phosphoric acid. One of these impurities, di-n-butyl hydrogen phosphate [and subsequently various homologues of the general formula $(RO)_2PO(OH)$], later found a use as powerful and selective reagents in solvent extraction.

Now the extraction of uranium from nitric acid by TBP depends primarily on a solvation effect in which the organic reagent replaces water from the component ions to form a less hydrophilic and uncharged complex, thus:

$$UO_2^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + 2TBP_{(0)} \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP_{(0)} + \text{water} \qquad (1)$$

Here the subscript (0) distinguishes material present in an immiscible organic phase from that present in the aqueous phase in contact with it.[1] On the other hand the extraction coefficient of uranium(VI) (at low concentrations) by a dialkyl hydrogen phosphate (which, like the TBP in the former process, is usually dissolved in an inert diluent such as kerosene, hexane or carbon tetrachloride) varies directly with the square of the concentration of the extractant in the organic phase and inversely with the square of the hydrion concentration. Since the reagent is known to be dimerized in an organic phase[2] the process has been interpreted by BAES *et al.* as follows:[3]



(2)

[1] H. A. C. MCKAY, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 314. United Nations (1956).
[2] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1277 (1957).
[3] C. F. BAES, R. A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).

Vol. 15 1960

Under comparable conditions the extraction coefficient for process (2) is greater than that for process (1) by a factor of 10^3 to 10^4.

It has recently been found that certain mixtures of non-ionic reagents of the type $(RO)_3PO$ with chelating agents of the type $(RO)_2PO(OH)$ give greater extraction coefficients for uranium than could have been anticipated from a consideration of the extraction coefficients for the individual processes (1) and (2). Furthermore the non-ionic component need not be a trialkyl phosphate, and the maximum extraction coefficient for mixtures of di(2-ethylhexyl) hydrogen phosphate and various types of neutral additives is found to increase in the order $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$ (R = n-butyl). BLAKE *et al.* state that "this synergistic enhancement of the extraction coefficient seems limited to dialkyl phosphoric acid–neutral reagent combinations" and, referring to the elements V, Th, Al, rare earths, Fe and U which they had studied, "uranium is the only metal . . . . . which extracts synergistically."[4]

We feel that these statements are too sweeping, for our own analysis of the problem of synergic enhancement of solvent extraction suggests that the phenomenon may be realised in a number of systems. The sufficient conditions* would appear to be that

(i) one of the active solvents is capable of neutralizing the charge on the metal ion, preferably by forming a chelated complex,
(ii) the second active solvent is capable of displacing any residual co-ordinated water from this formally neutral metal complex and rendering it less hydrophilic
(iii) the second active solvent is not in itself hydrophilic and is co-ordinated less strongly than the first (chelating) solvent,
(iv) the maximum co-ordination number of the metal and
(v) the geometry of the ligands are favourable.

Such considerations will explain why excess of 8-hydroxyquinoline (HOx) promotes the extraction of Sr^{2+} into chloroform as the solvated chelate complex $Sr(Ox)_2$, 2HOx whereas at lower concentrations of oxine the hydrophilic species $Sr(Ox)_2$, $2H_2O$ remains in the aqueous phase.[6] Similarly, magnesium can be precipitated from aqueous solution as the complex $Mg(Ox)_2$, $2H_2O$, but this cannot be extracted into chloroform. However the extraction does proceed under the combined influence of 8-hydroxyquinoline and n-butylamine which presumably displaces the co-ordinated water and renders the complex more hydrophobic.[7] The joint effect of salicylic acid and pyridine in promoting the extraction of copper into chloroform[8] can be explained in the same terms and a number of other examples can be found in the literature.[9]

Of particular relevance is the observation, made some years ago by CUNNINGHAME and co-workers, that the addition of tri-n-butyl phosphate increased the extraction of praseodymium and neodymium by solutions of 1,1,1-trifluoro-3-2′-thenoylacetone (TTA).[10] We therefore decided to use as a model system for testing our hypotheses the extraction of uranium from nitric acid by mixtures of TTA and TBP (or tri-n-butyl

* Synergism may appear in a system in which neither of the active solvents is a chelating agent (cf. ref. 5). The degree of synergic enhancement is altogether smaller and different considerations apply (*q.v.*).

[4] C. A. BLAKE, C. F. BAES, K. B. BROWN, C. F. COLEMAN and J. C. WHITE, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 28, p. 289. United Nations (1959).
[5] A. G. GOBLE and A. G. MADDOCK, *Trans. Faraday Soc.* **55**, 591 (1959).
[6] D. DYRSSEN, *Svensk. Kem. Tidskr.* **67**, 311 (1955).
[7] F. UMLAND and W. HOFFMAN, *Anal. Chim. Acta* **17**, 234 (1957).
[8] V. A. GORDIEYEFF, *Analyt. Chem.* **22**, 1166 (1950).
[9] D. DYRSSEN, *J. Inorg. Nucl. Chem.* **8**, 291 (1958).
[10] J. G. CUNNINGHAME, P. SCARGILL and H. H. WILLIS, AERE/C/M-215 (1954).

phosphine oxide, TBPO). It is well known that chelation by TTA (HX) promotes the extraction of uranium as the formally neutral species UO_2X_2.[11]

$$UO_2^{2+}{}_{(aq)} + 2HX_{(o)} \rightleftharpoons UO_2X_{2(o)} + 2H^+{}_{(aq)} \quad (3)$$

The extraction of uranium by TBP is formulated in equation (1). We now find, in agreement with prediction, that there is a remarkable synergic enhancement of solvent extraction when these two reagents are used in combination. As anticipated, the effect with tri-n-butylphosphine oxide is still larger.

EXPERIMENTAL

The physical properties of the 1,1,1-trifluoro-3-2′-thenoylacetone used in these experiments, viz. melting point (43–43·5°C) and molar extinction coefficient (11,900 at 330 mμ) concurred with those reported elsewhere.[12] The tri-n-butyl phosphate was purified as described in our earlier paper.[13] The tri-n-butyl phosphine oxide was purified by distillation, the fraction b.p. 300–305°C being used.

In the first series of partition experiments 0·02 M stock solutions of these reagents were made up in cyclohexane and mixtures were prepared as required. For the other experiments the solutions were prepared by direct weighing and dilution with cyclohexane.

The partition experiments were carried out by equilibrating 2 ml of the organic phase with 2 ml of the aqueous phase, which contained the necessary amount of tracer, for 24 hr on a shaker at room temperature (21–23°C). The aqueous phase used for these experiments was 0·01 N nitric acid and the total uranium concentration was $1·025 \times 10^{-4}$ M as ^{233}U. The uranium content of each phase was determined by taking aliquot portions, evaporating them down on to stainless steel disks and taking the usual precautions for the preparation of α-sources for counting.

RESULTS

The results for the partition of uranium between 0·01 M HNO_3 and mixtures of TTA and TBP of constant total molarity 0·02 M in cyclohexane are given in Table 1

TABLE 1.—THE DISTRIBUTION COEFFICIENTS OF URANIUM(VI) BETWEEN 0·01 N NITRIC ACID AND MIXTURES OF TTA AND TBP OR TBPO IN CYCLOHEXANE (0·02 M)

TBP or TBPO (%)	Distribution coefficient	
	TTA–TBP	TTA–TBPO
0	0·063	0·063
2·5	10·16	546
5	17·6	763
10	29·5	
20		854
30	56·2	894
45	65·9	
50		995
55	51·0	
60	42·8	
70	30·0	810
80	21·9	723
90	2·56	576
95	1·03	325
100	0·00057	38·55

[11] G. N. WALTON, F. BARKER and G. BYFLEET, AERE/C/R-768 (1951).
[12] R. A. DAY and R. M. POWERS, *J. Amer. Chem. Soc.* **76**, 3895 (1954).
[13] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **10**, 306 (1959).
[14] W. C. DAVIES and W. J. JONES, *J. Chem. Soc.* 33 (1929).

Vol. 15 1960

and shown in Fig. 1. When 20 per cent of the TTA has been replaced, a maximum synergic enhancement of 1000 is obtained. In other experiments it was shown that if 0·02 M TTA is made 0·01 M in TBP the partition coefficient increases from 0·06 for TTA alone to 300, which is a synergic enhancement of 5000. Similar experiments using mixtures of TTA and TBPO of constant total molarity 0·02 M (Table 1 and Fig. 1) showed that there was an enhancement of 10,000 when 10 per cent of the TTA had been replaced by TBPO.

Following the discovery of these large synergic effects a detailed examination of

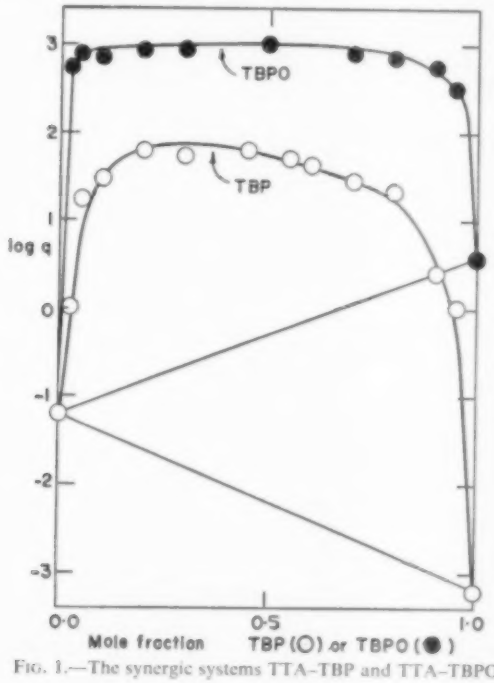


FIG. 1.—The synergic systems TTA–TBP and TTA–TBPO.

the two systems was undertaken. First the concentration of the TTA was maintained constant at 0·02 M (in cyclohexane) and the concentration of TBP in the solution increased in stages from 10^{-5} M to 0·02 M. The fraction of uranium extracted from 0·01 N HNO_3 into each of these mixed solutions was then measured radiometrically. The series of experiments were repeated, keeping the concentration of TTA constant at 0·01, 0·005 and 0·002 M while varying that of the non-ionic component (TBP) as before. The results of these experiments are shown in Fig. 2. A similar set of experiments were also carried out using TBPO in place of the TBP, Fig. 3. Then another series of experiments were carried out in which the concentration of TBP was held constant at selected values of 0·02, 0·01, 0·005 and 0·002 M whilst those of the chelating agent (TTA) were varied over the range 10^{-5} to 0·02 M (Fig. 4).

In previous papers [13,15] it has been shown that as long as a solute, S, does not associate with a metallic species in the aqueous phase,

$$\log q = \bar{S} \log [S] + \text{constant} \qquad (4)$$

[15] H. IRVING, F. J. C. ROSSOTTI, and R. J. P. WILLIAMS, *J. Chem. Soc.* 1906 (1955).

where q is the partition coefficient (assuming only one species is being extracted), [S] is the concentration of the solute, S, in the organic phase, and $\bar{S}$ is the average number of molecules of the solute associated with each molecule of the metallic species extracted into the organic phase, and is numerically the same as the gradient of the

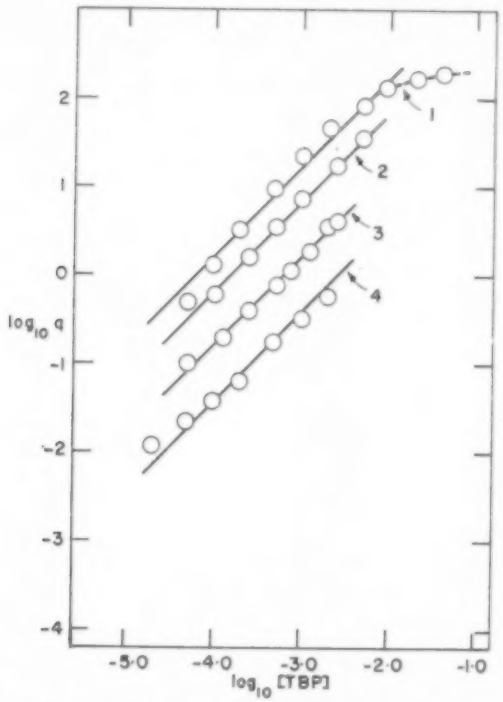


FIG. 2.—The variation in distribution coefficient when increasing concentrations of TBP are added to a fixed concentration of TTA ([TTA] > [TBP]). Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TTA.

plot of log q against log [S]. The solute, S, can be identified in turn with TTA, TBP, or TBPO.

In Fig. 2 lines of slope 1 have been drawn through the experimental points. These lines are a good fit for the most part, but deviations occur at very low ([TBP] $\leqslant$ [U]) and very high ([TBP] $>$ 0·02 M) concentrations of tri-n-butyl phosphate. The decrease of the values of the gradient when [TBP] $\leqslant$ [U] is understandable for there is then insufficient TBP present to transform all the uranium into the 1 : 1 complex, which appears to be formed at higher concentrations. The deviation when [TBP] $>$ 0·02 M is doubtless due to the increasing tendency for the two solutes (TTA and TBP) to associate. Such association, which is revealed by infra-red measurements, will decrease their effective individual concentrations: activity effects also become increasingly important at these concentrations.

From these results it would appear that only one mole of TBP is associated with each atom of uranium extracted. It remains to enquire whether the extracted species still retain the two molecules of TTA which are normally associated with each uranyl ion (equation 3). From the graphs shown in Fig. 2, the values of q for the

Vol. 15 1960

variation of the concentration of TTA at a fixed concentration of TBP can be obtained. These are shown in Fig. 5. The best lines drawn through these points are of slope 2. These results lead to the conclusion that the uranyl ion extracts as UO_2X_2, TBP from mixtures of TTA and TBP where [TTA] > [TBP].

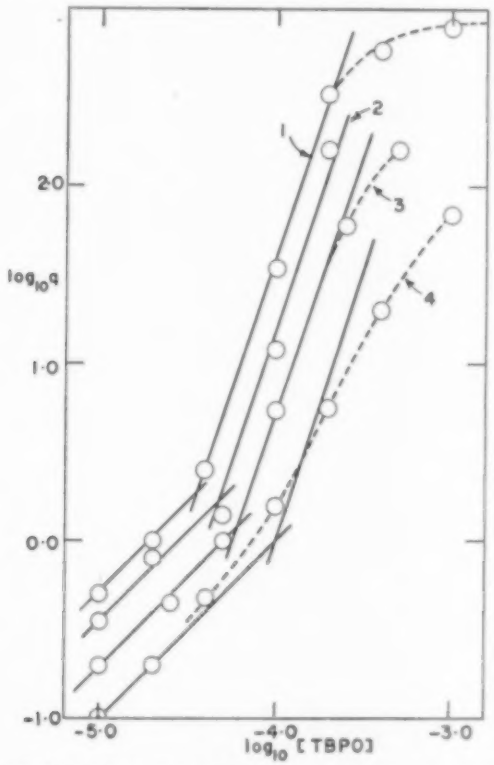


FIG. 3.—The variation in distribution coefficient when increasing concentrations of TBPO are added to a fixed concentration of TTA ([TTA] > [TBPO]). Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TTA.

We must now consider the situation where [TBP] > [TTA]. It is well known that uranyl nitrate is extracted into TBP as $UO_2(NO_3)_2$, 2TBP (equation 1), and the problem is to determine how the composition of the extracted species changes when a small amount of TTA is present. The results given in Fig. 4 show the variation of q with [TTA] at fixed [TBP]; and those in Fig. 6 (which were obtained from the graphs in Fig. 4) are for the variation of q with [TBP] at fixed [TTA].

By similar arguments to those used above, it can be seen that at low concentrations of TTA it would appear that there is one mole of TBP and one mole of TTA associated with each uranyl ion. With concentrations of TTA $> 2 \times 10^{-4}$ M, one mole of TBP and two moles of TTA are associated with each uranyl ion. As a condition for solvent extraction is that the species crossing the phase boundary should be formally neutral, it is reasonable to postulate that when [TTA] $< 2 \times 10^{-4}$ M the predominant extracted species is $UO_2(NO_3)X$, TBP, and when [TTA] $> 2 \times 10^{-4}$ M, its composition favours UO_2X_2, TBP.

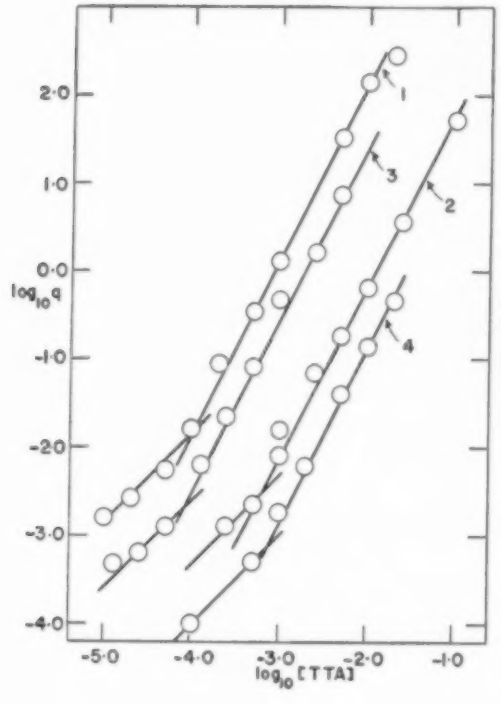


FIG. 4.—The variation in distribution coefficient when increasing concentrations of TTA are added to a fixed concentration of TBP ([TBP] > [TTA]). Curve 1. 0·02; Curve 2. 0·01; Curve 3. 0·005; Curve 4. 0·002 M TBP. Note: Curves 2 and 4 are displaced one log unit to the right for convenience in plotting.

Vol. 15 1960

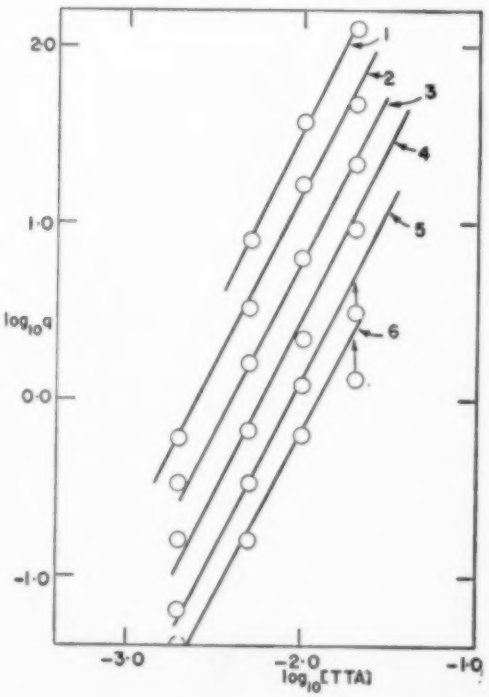


FIG. 5.—The variation in distribution coefficient when increasing concentrations of TTA are added to a fixed concentration of TBP ([TTA] > [TBP]). Curve 1. 5×10^{-3}; Curve 2. 2×10^{-3}; Curve 3. 10^{-3}; Curve 4. 5×10^{-4}; Curve 5. 2×10^{-4}; Curve 6. 10^{-4} M TBP.

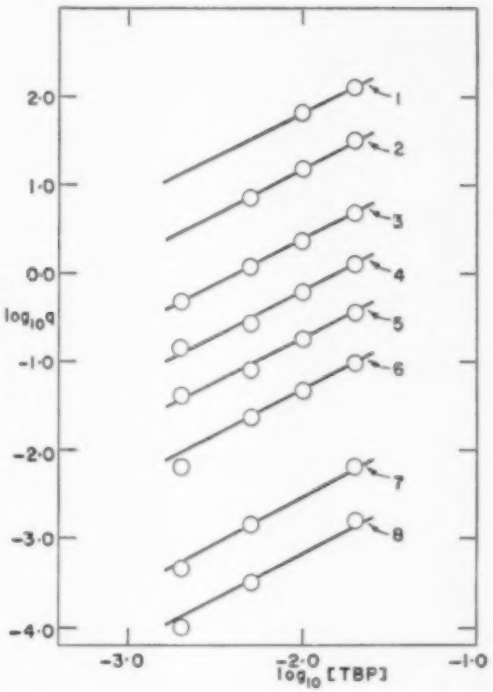


FIG. 6.—The variation in distribution coefficient when increasing concentrations of TBP are added to a fixed concentration of TTA ([TBP] > [TTA]). Curve 1. 0·01; Curve 2. 5×10^{-2}; Curve 3. 2×10^{-2}; Curve 4. 10^{-2}; Curve 5. 5×10^{-3}; Curve 6. 2×10^{-3}; Curve 7. 2×10^{-5}; Curve 8. 10^{-5} M TTA.

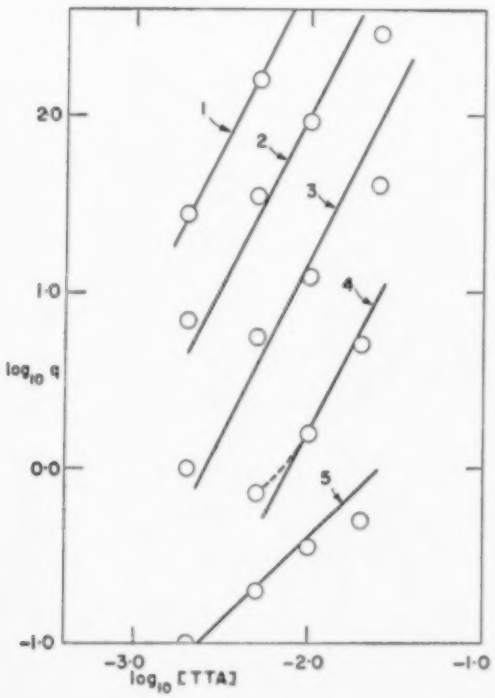


FIG. 7.—The variation in distribution coefficient when increasing concentrations of TTA are added to a fixed concentration of TBPO ([TTA] > [TBPO]). Curve 1. 5×10^{-4}; Curve 2. 2×10^{-4}; Curve 3. 10^{-4}; Curve 4. 5×10^{-5}; Curve 5. 10^{-5} M TBPO.

The results for TBPO are given in Fig. 3: at low concentrations of TBPO lines of slope 1, and at higher concentrations of TBPO of slope 3, give the best fit to the experimental points. The points plotted in Fig. 7, for the variation of q with [TTA] at fixed [TBPO], were obtained from the graphs in Fig. 3. The best lines for these points were of slope 2. The deviations at higher concentrations of TBPO can be interpreted by similar arguments to those put forward earlier for TBP. It is reasonable to postulate that when [TBPO] $< 5 \times 10^{-4}$ M, the extracted species is UO_2X_2, TBPO, and that when [TBPO] $> 5 \times 10^{-4}$ M, it is UO_2X_2, 3TBPO.

All the results can be represented by a general equation,

$$UO^{2+}_{2(aq)} + 2HX_{(0)} + xS_{(0)} \rightleftharpoons UO_2X_2S_{x(0)} + 2H^{+}_{(aq)} \qquad (5)$$

for which values of the mixed equilibrium constant, K, may be calculated:

$$K = \frac{[UO_2X_2S_x]_{(0)}[H^+]^2_{(aq)}}{[UO_2^{2+}]_{(aq)}[HX]^2_{(0)}[S]^x_{(0)}} \qquad (6)$$

where (0) and (aq) refer to the organic and aqueous phases respectively, for S = TBP $x = 1$; for S = TBPO, $x = 3$; and for the extraction of the uranyl ion by TTA alone $x = 0$. The values of K calculated from the experimental results are for S = TBP, $\sim 10^{3\cdot9}$ (for both high and low concentrations of TTA): for S = TBPO, $10^{14\cdot4}$; and for UO_2X_2 itself, $10^{-2\cdot8}$. This value for UO_2X_2 compares favourably with the values obtained by WALTON of $10^{-2\cdot5}$,[11] and by American workers (in perchloric acid medium of $10^{-2\cdot76}$.[16]

DISCUSSION

Two different explanations for the synergic effect in the system $(RO)_2PO(OH)$ and $(RO)_3PO$ (or R_3PO) have been proposed. Since the dialkylphosphoric acids exist in organic solutions almost exclusively as dimers,[2,3] BLAKE *et al.*[4] formulate the complex with uranium(VI) as in equation (2) above, where uranium has a co-ordination number of six. The synergic enhancement of extractive power is then attributed to the addition, through hydrogen bonding, of one molecule of the neutral reagent to this uranyl–dialkylphosphate complex, thus:

$$UO_2Y_4H_2 + R_3PO = UO_2Y_4H_2 - - - OPR_3 \qquad (7)$$

(where HY represents a dialkylphosphoric acid). They do not, however, indicate why this would necessarily lead to a higher extraction coefficient. The decrease in extraction beyond the maximum is attributed to increasing interaction by hydrogen bonding between the acidic and neutral extractants.

As an alternative explanation, KENNEDY[17] suggests that the reaction between the uranyl ion and the dimerized dialkylphosphoric acid produces an eight-co-ordinated complex:

$$UO_2^{2+} + 2(HY)_2 \rightleftharpoons \left[(RO)_2(OH)P{=}O \longrightarrow\right]_2 UO_2 \left[\begin{matrix} O \\ \diagup \quad \diagdown \\ P(OR)_2 \\ \diagdown \quad \diagup \\ O \end{matrix}\right]_2 + 2H^+ \qquad (8)$$

He stresses the fact that the free energy change for the dimerization of the dialkylphosphoric acid is ~ -8000 cals/mole, so that provided a molecule of TBP (or TBPO, etc.)

[16] U.S.A.E.C.D. CC-3618.
[17] J. KENNEDY, AERE/C/M 369-(1958).

Vol. 15 1960

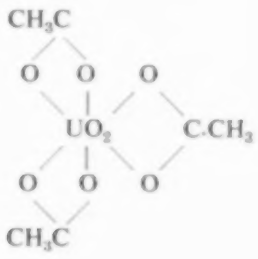
associates as strongly, or more strongly than a molecule of a dialkylphosphoric acid (considered now as a neutral-, as opposed to the chelating-component), there should be a nett decrease in free energy as the reaction

$$UO_2^{2+} + (HY)_2 + 2TBP = UO_2Y_2, 2TBP + 2H^+ \quad (9)$$

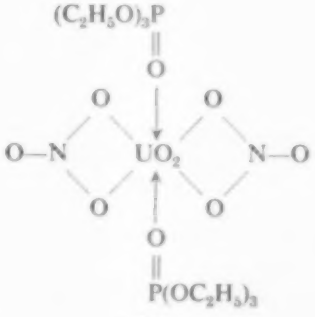
proceeds from left to right. This would certainly favour the formation of the postulated eight-co-ordinated complex and by implication the percentage of uranium extracted. This explanation assumes that two molecules of TBP etc. are associated with each atom of uranium. BLAKE's equation [(7) above] and the published data (ref. 4, Fig. 3) do not suggest that more than one molecule of the neutral component is involved. KENNEDY agrees with BLAKE's explanation of the decrease in the extraction coefficient beyond the synergic maximum.

BLAKE notes, without explanatory comment, that the phosphinic acids tested showed no synergic enhancement and that "an immediate decrease in extraction ability is observed when neutral reagents are combined with monoalkylphosphoric acids". The addition of TBP to di(2-ethylhexyl)phosphinic acid also produced a small but definite decrease in extraction. KENNEDY regards these results as a natural consequence of the expected solvation order $(n\text{-}C_4H_9O)_3PO \ll R_2PO(OH)$.

That the co-ordination number of uranium(VI) can rise to eight has been established by X-ray crystallography for the triple acetate, $Na[(UO_2)(OAc)_3]$[18] and for the complex $UO_2(NO_3)_2$, $2(C_2H_5O)_3PO$[19] whose basic structures are shown below (III and IV).



(III)



(IV)

However, while SACCONI's studies of the infra-red spectra of complexes of uranium (VI) with β-diketones have provided abundant evidence that these are co-ordinatively unsaturated, it appears that they generally form adducts with only one molecule of water, ammonia, pyridine, etc., and that this extra molecule is co-ordinated directly to the central metal atom thus producing seven-co-ordinate uranium. The failure to form eight-co-ordinated complexes in these cases may well be due to steric factors which will be even more pronounced with certain of the neutral phosphorus compounds now under discussion.[20]

In view of SACCONI's observations, the formation of an adduct UO_2X_2, TBP (where HX = TTA) is scarcely a matter for surprise. WALTON's work[11] suggests that the complex of uranyl ion with TTA contains at least one molecule of water, but

[18] W. H. ZACHARIASEN and H. A. PLETTINGER, *Acta. Cryst.* **12**, 526 (1959).
[19] J. E. FLEMING and H. LYNTON, *Chem. & Ind.* 1408 (1959).
[20] L. SACCONI and G. GIANNONI, *J. Chem. Soc.* 2751 (1954).

the analytical data is not sufficiently extensive to make a more precise statement. If the TBP has displaced water from this more hydrophilic adduct according to the equation

$$(UO_2X_2, H_2O)_{(o)} + TBP_{(o)} \rightleftharpoons (UO_2X_2, TBP)_{(o)} + H_2O_{(aq)} \qquad (10)$$

the synergic effect can readily be explained. The existence of a 1 : 1 complex of uranyl bis(1,1,1-trifluoro-3-2′-thenoyl-acetonylate) and tri-n-butyl phosphate has been confirmed spectrophotometrically in solutions as dilute as 4×10^{-3} M and in the presence of a large excess of the latter.[21]

The tendency of strontium oxinate to take up molecules of unionized 8-hydroxyquinoline in place of water (see above, ref. 6) appears to be paralleled by that of the uranyl–TTA complex to take up one molecule of unionized TTA in concentrated solution of this reagent (spectrophotometric evidence only).[22]

It is significant that KENNEDY's explanation of synergism in systems involving dialkylphosphoric acids etc. (see above), which rests essentially upon their extensive polymerization in organic solutions, cannot readily be extended to the present case, for there is no evidence for the dimerization of TTA under comparable conditions. On the other hand, the explanation of synergism as an effect due to the displacement of solvated water by a more strongly co-ordinated and less hydrophilic molecule can readily be extended to all the cases so far reported.

The synergic enhancement of the solvent extraction of UO_2^{2+} by TTA–TBP mixtures also occurs at higher concentrations of uranium (up to 10^{-2} M) and of TTA (up to 0·2 M).[21] It has been shown that when TTA is added to a solution of UO_2X_2 in benzene there is a small increase in the molar extinction coefficient at $\sim$500 mμ, which has been interpreted by ORR as due to the formation of an adduct UO_2X_2, HX; its concentration is estimated as about 60 per cent when the concentration of TTA is 1·045 M.[23] However the replacement reaction

$$(UO_2X_2, HX)_{(o)} + HX_{(o)} \rightleftharpoons (UO_2X_2, TBP)_{(o)} + HX_{(o)} \qquad (11)$$

would not immediately explain the synergic effect unless the TBP adduct has a higher partition coefficient than the adduct with TTA. In any case the evidence is that over the range 0·01 M $<$ [TTA] $<$ 1·0 M, the sole species extracted into the benzene phase is simply UO_2X_2.[23,24]

It is of interest to compare the properties of analogous chelate complexes of uranium(IV) and uranium(VI). The latter, UO_2X_2, are usually co-ordinatively unsaturated, sparingly soluble in non-polar solvents such as benzene, hexane, chloroform and carbon tetrachloride, but more soluble in solvents containing oxygen (or nitrogen) atoms capable of electron donation. On the other hand, chelate complexes of uranium(IV), of general formula UX_4, are normally co-ordinatively saturated (C.N. = 8), readily soluble in non-polar solvents, but only sparingly soluble in methanol or ether. MARTELL and CALVIN[25] attribute these differences to direct co-ordination between the polar solvent and the central metal atom, rather than by

[21] H. IRVING and K. THOMSON. To be published.
[22] E. L. KING, U.S.A.E.C. TID-5290 Bk. 1, p. 269 (1958).
[23] W. C. ORR, U.S.A.E.C. UCRL-196 (1948).
[24] D. L. HEISIG and H. W. CRANDALL, U.S.A.E.C. UCRL-764 (1950).
[25] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds* p. 243. Prentice Hall, New York (1952).

Vol. 15 1960

polar interaction or hydrogen bonding between solvent molecules and attached groups: this can only occur when the central metal atom is co-ordinatively unsaturated as in complexes of UO_2^{2+}. In complexes of uranium(VI) with β-diketones the uranium atom appears to have a co-ordination number greater than six, but less than eight. If the "extra" molecule is one of water, the complex as a whole will be somewhat hydrophilic and not readily soluble in non-polar solvents. If, however, the water can be replaced by another less hydrophilic donor molecule the position may be reversed. On this basis a clearer picture of synergism can be painted, at least for the solvent extraction of uranium(VI). This could be generalized in the following terms.

Consider a metal ion, M^{n+}, of maximum co-ordination number N. Assume that it reacts with a chelating agent, HX, to give a formally neutral species, MX_n, which takes up water to complete its co-ordination shell. The hydrated complex MX_n, $(N\text{-}2n)H_2O$ (assuming HX is a bidentate ligand) may be sufficiently hydrophilic to ensure a greater solubility in water than in a non-polar solvent and this in any event will favour a low extraction coefficient. If however a second donor molecule (the "neutral" or "non-ionic" component, S) is present, some or all of this water may be displaced,

$$MX_n, (N\text{-}2n)H_2O + xS = MX_n, (N\text{-}2n\text{-}x)H_2O, xS + xH_2O \qquad (12)$$

the resulting complex will be less hydrophilic and more readily extracted. In this simplest statement of the situation, replacement of water by the "neutral component" is presented as a displacement molecule for molecule. This need not, and probably would not be the case: for the co-ordination of a single, bulky organic ligand in place of a single water molecule will have a more far-reaching effect on the solvation number due to the extensive disruption of the hydration "iceberg" that has been formed through hydrogen bonding.

When $2n + x = N$ the complex will be non-hydrated and co-ordinatively saturated: it should be unable to form a higher solvate unless further donor molecules can be attached through some site other than the central atom, e.g. through hydrogen bonding elsewhere. If $N > 2n$ (for a bidentate chelating agent), a synergic effect should be possible provided the geometry of the metal complex can be adapted to accommodate the additional donor molecules (water or "neutral components"). By the same reasoning no synergic effect would be anticipated in the extraction of uranium(IV) by a combination of bidentate chelating agents and neutral ligand species since the complex UX_4 would already be co-ordinatively saturated.

If 4*f* electrons can participate in bonding complexes of the lanthanons, as 5*f* electrons are thought to do in the actinides, synergic enhancement of solvent extraction should be detectable among the rare earths, although the effect would probably be smaller. This could account for the synergic effect in the system Nd (or Pr)–TTA–TBP noted by CUNNINGHAME[10]. Indeed it is tempting to predict that synergic effect may be found among trivalent lanthanides and trivalent, pentavalent, and hexavalent actinides, but not with tetravalent rare earths or actinides since their complexes would already be co-ordinatively saturated.

Synergic effects are well known in many biochemical systems where the association of two drugs, two insecticides, two germicides, or a toxic and a non-toxic component exert effects which could not have been predicted from the behaviour of the substances considered severally. No general explanation of such complex phenomena has been

given and indeed no such universal explanation is to be expected, for, to take a special case, particular physiological symptoms may be produced by several different stimuli. For similar reasons we would not suppose that all cases of synergic enhancement of solvent extraction will be explicable in the same terms, even using the rather general model we have proposed above. Thus MADDOCK's remarkable discovery of synergism in the solvent extraction of protactinium from concentrated hydrochloric acid into mixtures of diisopropylketone and diisopropylcarbinol, or of diisopropylcarbinol and solvents of high dielectric constant such as nitromethane, nitrobenzene, and benzonitrile, would appear to require a different treatment.[5] LEWIS, working in these laboratories,[26] has also observed synergic enhancement in the extraction of indium from hydrochloric acid into a variety of mixtures of organic solvents. It is noteworthy that for both these metals the extracted species is an acido-complex (e.g. $HInCl_4$) and that variations in the co-ordination number of the metal are unlikely to be of great significance. On the other hand the acido-complexes will be solvated by varying amounts of water and the two organic solvents. It is thus possible, even here, to picture a co-operative effect through which the solvent–solvent interaction has produced a less hydrophilic acido-complex while, at the same time, creating an immiscible organic phase more favourable to its reception. The precise explanation of such synergic effects, which appear to be altogether more subtle and specific, must await a more complete physico-chemical investigation of the very complex equilibria involved.

Acknowledgements—We are indebted to the United Kingdom Atomic Energy Authority (A.E.R.E.) for financial support and the loan of equipment. We should also like to thank Dr. E. GLUECKAUF for his assistance and helpful discussion. The above work forms part of the subject of a Patent Application by the U.K.A.E.A.

[26] H. IRVING and D. C. LEWIS. To be published.

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 171 to 176. Pergamon Press Ltd. Printed in Northern Ireland

THE INFLUENCE OF DILUENT POLARITY ON THE EXTRACTION OF NEPTUNIUM AND URANIUM COMPOUNDS TO ORGANIC MEDIA

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(*Received* 14 *September* 1959)

Abstract—The influence of polarity in two-component diluent mixtures of chloroform, benzene and carbon tetrachloride on the extraction of uranium(VI) and neptunium(IV) and (VI) complexes with tri-n-butylphosphate, tetrabutylammonium nitrate and trilaurylamine has been studied. The results are interpreted in terms of the size of the complex, the diluent structure and the energy of hole formation in the organic phase on the one hand, and the dipole interaction between complex and diluent on the other hand.

IT has been established that the polarity of the diluent has an important influence on the extraction of plutonium compounds into an organic medium from an aqueous phase.[1] The influence of the dielectric constant and the polarity has also been examined in the case of the extraction of uranium[2,3] and protactinium.[4]

In the present work it was intended to examine the following problems; the influence of diluent polarity on the extraction of other actinide elements in different oxidation states, and the influence of the structures of the extracting agent on the extraction process. Hexavalent uranium and tetra and hexavalent neptunium were used. Apart from tributyl phosphate (TBP), the complexing agents were a quaternary amine with short carbon chains, quaternary butylammonium nitrate, (TBAN) in HNO_3 and a tertiary amine with long chains, trilaurylamine (TLA) in H_2SO_4.

EXPERIMENTAL

Aqueous solution of ^{233}U and ^{237}Np were used, of initial concentration (i.e. before extraction) ca. $2{\cdot}5 \times 10^{-5}$ M ^{233}U and 2×10^{-4} M ^{237}Np. The ^{233}U was obtained from the laboratories of C.E.A., France, and the ^{237}Np from ORNL, USA, (Pu content < 1 p.p.m., U < 10 p.p.m., Am $< 0{\cdot}1$ p.p.m.).

The concentrations of extracting agents in the organic phase were chosen so as to fulfil the following conditions:

(1) the concentration of extracting agent should be as low as possible, so that the organic phase is composed predominantly of the diluents, which are themselves incapable of extracting,

(2) the concentration of extracting agent must be lower than the limit set by its solubility (important for TBAN in CCl_4) to avoid the formation of a third phase rich in the extracting agent,

(3) the concentration of extracting agent should ensure a partition coefficient in the range 0·05–3, to reduce experimental errors. The concentration of extracting agents chosen were 0·15 M for TBP, 0·01 M for TBAN and 0·015 M for TLA.

Carbon tetrachloride, n-hexane, cyclohexane and benzene were used as non-polar diluent and chloroform and bromoform as polar diluents.

* Work done in the Centre d'Etudes Nucleaires, Saclay, France, while holding a Fellowship of the International Atomic Energy Agency.

[1] M. TAUBE, *J. Inorg. Nucl. Chem.* **12**, 174 (1959).
[2] Z. I. DIZDAR *et al.*, *Bull. Inst. "Boris Kidrich"* **8**, 150, 59 (1958).
[3] V. B. SHEVTCHENKO *et al.*, *Radiokhimia* **3**, 257 (1959).
[4] A. G. GOBLE and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **7**, 94 (1958).

Before extraction the aqueous phase was 3–6 M in HNO_3 using TBP and TBAN, or ca. 0·5 M in H_2SO_4 for TLA.

Neptunium was oxidized to Np(VI) with 0·1 M $KBrO_3$ in 1 M HNO_3 or H_2SO_4, by heating for 30 min at 50°C.

In some cases oxidation was done at room temperature with 0·001 M $KMnO_4$ solution. Neptunium was reduced to Np (IV) with 0·9 M NH_2NH_2 and 0·18 M KI in 5 M HCl, by heating to 80°C for 60 min. In some cases of extraction with TLA, reduction was accomplished by means of freshly prepared $FeSO_4$ solution.

Radiometric estimation were done as previously described,[1] the phases being separated by spinning. Corrections were not applied for changes in phase volume or for self-absorption in sample layers during alpha activity measurements.

The ratio of the specific α-activity of the organic phase to the specific α-activity of aqueous phase for equal phase volumes, will be called the partition coefficient.

RESULTS

Results are shown in Figs. 1–8. To avoid plotting all experimental points only the best fitting curves from measurements in both phases, are shown in the figures. Fig. 9 summarizes the results of extraction with TBP using chloroform–benzene mixtures.

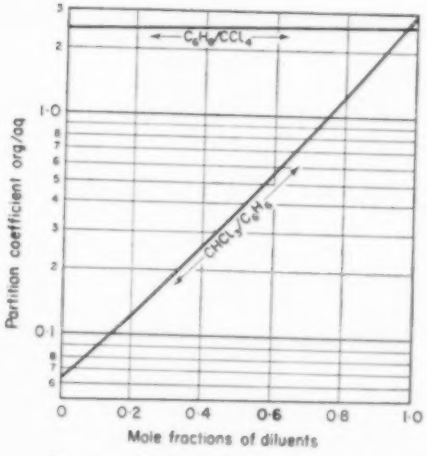

FIG. 1.—Uranium(VI) extraction with TBP from 5 M HNO_3 into diluent mixtures.

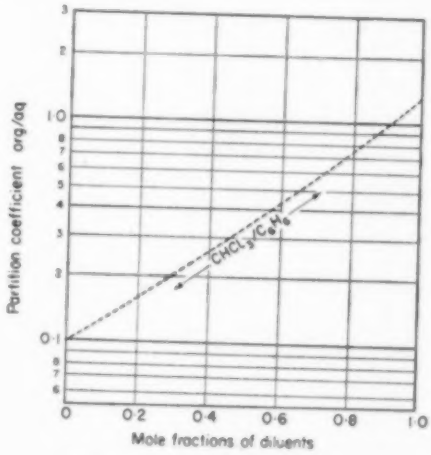

FIG. 2.—Neptunium(VI) extraction with TBP from 5 M HNO_3 into diluent mixtures.

Included in this figure are the results for Pu(IV) previously obtained.[1] The partition coefficient for extraction with benzene is greater than that for chloroform; in the case of the hexavalent metals UO_2^{2+} NpO_2^{2+}, twenty to thirty times, and in the case of tetravalent metals Pu^{4+} Np^{4+}, four to five times greater. It should be noted that the difference in the absolute values of the partition coefficient for Np^{4+} and Pu^{4+} is due in part to the difference in the concentrations of TBP, HNO_3 etc.

Fig. 10 summarizes the results of extraction with TBAN using chloroform–benzene mixture. Included in this figure are results for Pu(IV).[1] The appearance of distinct maxima for the partition coefficient in the chloroform–benzene mixtures should be noted for the tetravalent states; Np^{4+} Pu^{4+}. The ratio of the partition coefficient for a 1 : 1 benzene–chloroform mixture to the partition coefficient for pure chloroform

[1] M. TAUBE. *Nukleonika* In press.

Vol. 15 1960

is 8–10. In the case of the hexavalent states, UO_2^{2+} NpO_2^{2+}, however, there is no maximum (Fig. 11).

Fig. 12 summarizes results for Np(VI) extraction with TBAN from 3 M HNO_3 and with TLA from 0·5 M H_2SO_4. In a mixture of polar and non-polar diluents the

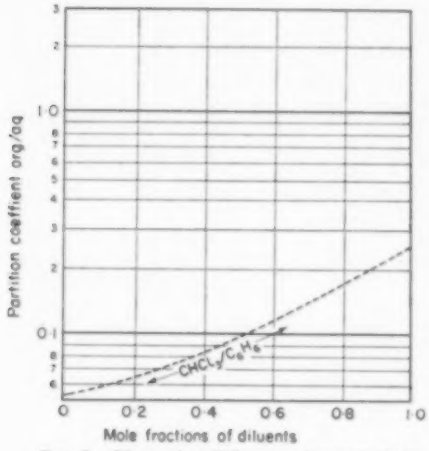

FIG. 3.—Neptunium(IV) extraction with TBP from 5 M HNO_3 into diluent mixtures.

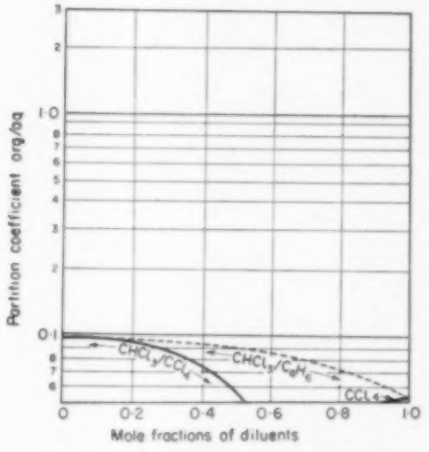

FIG. 4.—Uranium(VI) extraction with TBAN from 6 M HNO_3 into diluent mixtures.

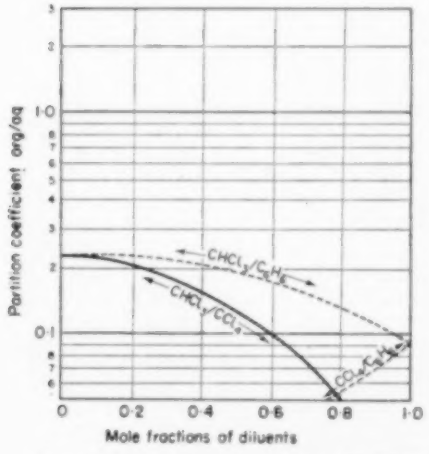

FIG. 5.—Neptunium(VI) extraction with TBAN from 3 M HNO_3 into diluent mixtures.

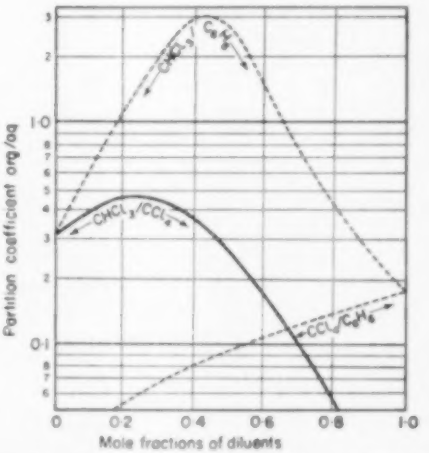

FIG. 6.—Neptunium(IV) extraction with TBAN from 3 M HNO_3 into diluent mixtures.

greater value of the partition coefficient is achieved with a more polar medium with TBAN and with a less polar medium with TLA.

For the chloroform–benzene system, the greatest extraction with TBAN occurred in pure chloroform, for which the partition coefficient is 2·5 times greater than for pure benzene. In the same system of diluents with TLA, maximal extraction occurred with benzene and minimal with chloroform, the partition coefficient for benzene being more than twenty times greater than for pure chloroform.

In the case of the carbon tetrachloride–benzene system maximal extraction with

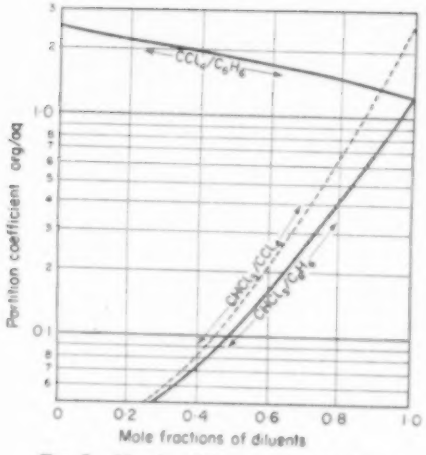

FIG. 7.—Uranium(VI) extraction with TLA from 0·5 M H_2SO_4 into diluent mixtures.

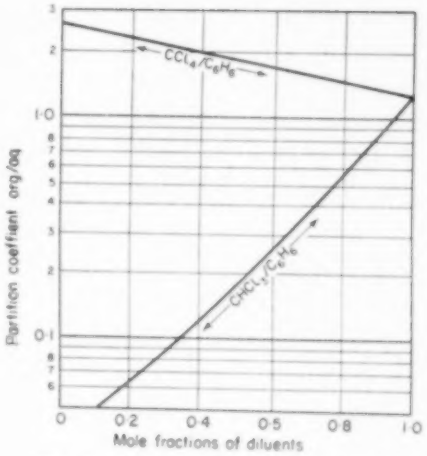

FIG. 8.—Neptunium(VI) extraction with TLA from 0·5 M H_2SO_4 into diluent mixtures.

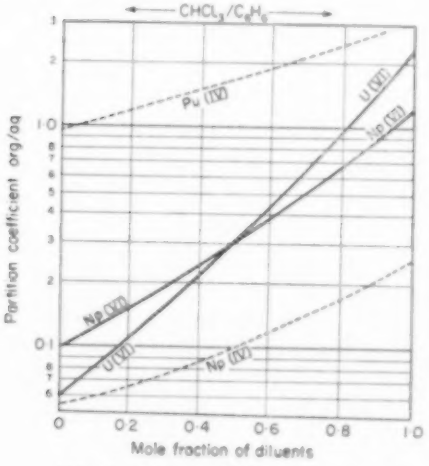

FIG. 9.—Plutonium(IV), neptunium(IV), neptunium(VI) and uranium(VI) extraction with TBP from HNO_3 into chloroform–benzene mixtures.

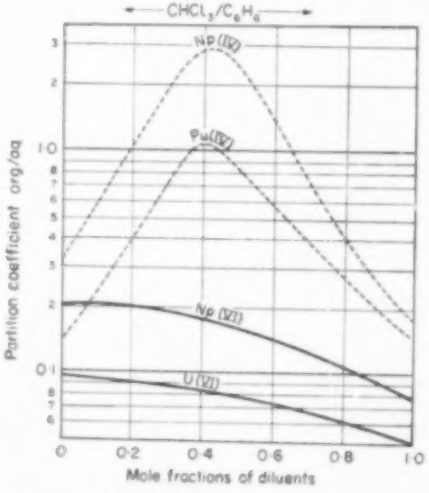

FIG. 10.—Plutonium(IV), neptunium(IV), neptunium(VI) and uranium(VI) extraction with TBAN from HNO_3 into chloroform–benzene mixtures.

TBAN occurs with benzene and the partition coefficient declines as the system is progressively diluted with carbon tetrachloride. In this system of diluents with TLA, the partition coefficient rises with progressive dilution with carbon tetrachloride.

It should be noted, however, that in the case of the extraction of TBAN–Pu (IV) in the chloroform–benzene system the maximum of extraction shifts towards the benzene end of the abscissa as the nitric acid concentration is increased.[5]

DISCUSSION

The above results can be explained on the basis of a relatively simple mechanism involving the following factors:

Vol. 15 1960

(1) Interaction between the dipole of the organic complex and the diluent dipoles, the strength of interaction being proportional to the product of the effective dipole moment of the extracted complex, and the dipole moment of the polar or polarizable constituent of the diluent mixture, multiplied by its mole fraction. Such an interaction obviously favours extractability of the complex.

(2) Mutual interaction between permanent or dispersion dipoles in the diluent mixture giving rise to the structure of the organic phase, which will impede the transfer

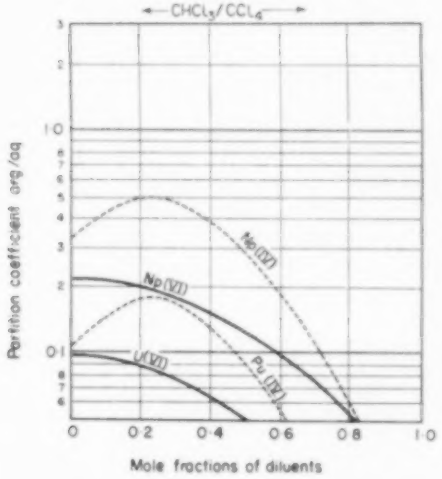

FIG. 11. — Plutonium(IV), neptunium(IV), neptunium(VI) and uranium(VI) extraction with TBAN from HNO_3 into chloroform–carbon tetrachloride mixtures.

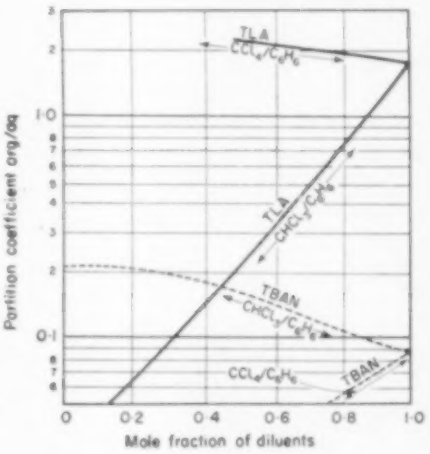

FIG. 12.—Neptunium(VI) extraction with TBAN (from HNO_3) and TLA (from H_2SO_4) into chloroform–benzene and benzene–carbon tetrachloride mixtures.

of the complex molecules (or ion-pairs) from the aqueous to the organic phase. The negative free energy connected with hole formation by extracted complex will be a function of the dipole moments permanent or induced of the diluent components and their mole fractions, and the dimensions of the extractable molecule. The energy of hole formation in the polar component will not usually decline linearly upon increasing dilution with a non-polar or less polar component, the energy curve being generally convex towards the abscissa of mole fraction. This follows from simple consideration of the marked break down of the liquid structure which can be expected as soon as relatively few non-polar molecules are introduced. For a chloroform–benzene mixture it has been found that the dielectric constant is not a linear function of composition, the curve being convex to the abscissa of composition.[6] This is in complete agreement with the above supposition.

For the type of complex dealt with here, as a first approximation one can assume that in most cases the hole size, and therefore magnitude of the corresponding free energy term will increase with increase in the number of atoms in the complex molecule or ion-pair. The hole size can be expected to be a simple power function of the number of atoms in the complex with an exponent less than unity.

Clearly the larger the size of complex molecule the more unfavourable for extraction

[6] J. HURWIC and E. MICHALCZYK, *Eighth Mendeleyev Congress of General and Applied Chemistry*. U.S.S.R. Academy of Sciences, Moscow (1959).

into a polar diluent system, this unfavourable effect being relatively greater in two-component systems the larger the mole fraction of the more polar component.

On the basis of the above assumptions, using likely values for the dipole moments and molecular dimensions of the complexes and for the induced dipole moment of benzene, and by suitably adjusting the numerical value of the ratio of the positive and negative free energy terms arising from factors (1) and (2) above, it is possible to derive an expression[7] which gives a good approximation to all the curves for the partition coefficient shown in this work and some of the data in previous works.[8–10]

Some of the gross results of this treatment are as follows:

(1) For complexes of strong dipole moment and relatively small dimensions (e.g. M (IV) complexes with TBAN), extraction should be much better into chloroform than into carbon tetrachloride, other things being equal. This is in fact the case as can be seen in Fig. 6. In a chloroform–benzene mixture one can expect better extraction than into either pure chloroform or benzene, because of the favourable interaction of the complex with benzene (resulting from dipole induction) and with chloroform together with destruction of the pure chloroform structure by the benzene (benzene structure is weaker since it is only due to disperse dipoles). Once again this expectation is borne out by the data of Fig. 6. Pure benzene and chloroform should give comparable extraction, as is in fact the case (Fig. 6).

(2) For complexes of small dipole moment and relatively large dimensions (e.g. M (VI) complexes with TLA), extraction should be much better into carbon tetrachloride than into chloroform other things being equal. Figs. 7 and 8 confirm this expectation. In a chloroform–benzene mixture no maximum in extraction is to be expected and the extraction into benzene should be better than to chloroform. This is because the hole formation energy term is decisive for a large complex. Fig. 7 shows the expected behaviour.

(3) For a complex of small dimensions and small dipole moment (e.g. TBP complexes with M (VI)), of dipole moment $3{\cdot}1 \times 10^{-18}$[3] extraction should be progressively greater (but of the same order of magnitude) in the following series; chloroform $<$ carbon tetrachloride $<$ benzene. Benzene gives better extraction than carbon tetrachloride because the favourable free energy term resulting from solvation is enhanced by the dipole induced in benzene by the TBP dipole and is greater than the unfavourable term resulting from the weak benzene disperse dipole structure. Data from[1] does not strictly confirm these expectations for carbon tetrachloride–benzene, but expectation for pure benzene and pure carbon tetrachloride are confirmed by.[3]

(4) For a complex of zero dipole moment and medium dimensions, (e.g. M (IV) complexes with DBP) extractability is decided only by the case of hole formation in the diluent i.e. extraction should increase in the series chloroform $<$ benzene $<$ carbon tetrachloride as is in fact found in.[1]

Acknowledgement—I would like to thank Mr. A. CHESNÉ for making possible the completion of the present work in the laboratory of the Service du Plutonium, Centre d'Etudes Nucleaires, Saclay, France, and Miss M. MOMMEJA for skilled technical assistance.

[7] M. TAUBE, Doctors Dissertation, Institut of Nuclear Research, Polish Academy of Science, Warsaw, October, 1959.
[8] C. F. COLEMAN, K. B. BROWN, T. G. MORRE and K. A. ALLEN, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, p. 510. United Nations (1959).
[9] A. S. WILSON, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, p. 544. United Nations (1959).
[10] M. SIEKIERSKA, *Roczniki Chem.* **32**, 1369 (1958).

Vol. 15 1960

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IONENAUSTAUSCH IN LÖSUNGSMITTELGEMISCHEN—III

ÜBER DIE VERTEILUNG DES THORIUMCHLORIDS ZWISCHEN SEINEN ALKOHOLISCHEN SALZSAUREN LÖSUNGEN UND STARK BASISCHEN ANIONENAUSTAUSCHERN

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(*Received* 11 *September* 1959)

Abstract—The present work tries to prove the existence of negatively charged chloride complexes of thorium. Since it is a well known fact, that in aqueous solutions containing hydrochloric acid no such complexes are formed, we have substituted different alcohols of the aliphatic series for water. Through the measurements of the distribution coefficients at different acidities of hydrochloric acid and at varying concentrations of alcohols we have concluded, that the adsorption of thorium on strongly basic anion exchangers is very high when the alcohol is present in a very high percentage. At the same time the effect of the amount of hydrochloric acid present i.e. the overall acidity of the solution, turned out to have no effect on the adsorption of thorium on these exchangers. By means of column operations we could verify our batch experiments, which led to the determination of the distribution coefficients and an adsorption isotherm.

1. EINLEITUNG

OBWOHL das Thorium als negativ geladener Nitrat[1-2] und Sulfatkomplex[3-4] aus salpetersauren bzw. ammoniumsulfathaltigen wässrigen Lösungen von stark basischen Anionenaustauschern adsorbiert wird, ergaben alle in salzsauren wässrigen Lösungen durchgeführte Untersuchungen, dass das Thorium wegen seiner geringen Tendenz negativ geladene Chloridkomplexe zu bilden, selbst aus konz. Salzsäure nicht von stark basischen Harzen adsorbiert wird.[5-6] Das vierwertige Uran dagegen wird aus salzsauren Lösungen höherer Konzentration ziemlich gut von derartigen Anionenaustauschern adsorbiert.[6] Dies ist umso bemerkenswerter, als sich das Thorium in der Regel analog zum vierwertigen Uran verhält und wie dieses einen dem Uran an Stärke vergleichbaren ersten Chloridkomplex $(ThCl)^{3+}$ bildet.[7]

Aus früheren von uns mit Thorium und Uran durchgeführten Versuchen ging hervor, dass die Adsorption dieser Elemente aus mineralsauren äthylalkoholischen Lösungen an stark basischen Ionenaustauschern wesentlich höher war als aus mineralsauren wässrigen Lösungen. Dennoch war die Adsorption des Thoriums aus salzsauren 80 Prozent Äthanol enthaltenden Lösungen nur sehr gering.

* Meinem verehrten Lehrer Herrn Prof. Dr. F. HECHT anlässlich seiner Ernennung zum Institutsvorstand herzlichst gewidmet.

(1) J. DANON, *J. Inorg. Nucl. Chem.* **5**, 237 (1958).
(2) D. J. CARSWELL, *J. Inorg. Nucl. Chem.* **3**, 384 (1957).
(3) N. SAITO und T. SEKINE, *Bull. Chem. Soc. Japan* **30** (5), 561 (1957).
(4) I. L. JENKINS und R. A. RICHARDSON, AERE/C/R 1217 (1953).
(5) E. K. HYDE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 281. United Nations (1956).
(6) K. A. KRAUS, G. E. MOORE und F. NELSON, *J. Amer. Chem. Soc.* **78**, 2692 (1956).
(7) W. C. WAGGENER und R. W. STAUGHTON, *J. Phys. Chem.* **56**, 1 (1952).

In der vorliegenden Arbeit wurden die Verteilungskoeffizienten des Thoriums, sowie eine Adsorptionsisotherme bei wesentlich höheren Alkoholkonzentrationen bestimmt. Aus diesen Untersuchungen ging hervor, wie im Folgendem gezeigt werden wird, dass das Thorium bei sehr hohen Konzentrationen an aliphatischen Alkoholen aus salzsauren Lösungen dieser Alkohole sehr fest von stark basischen Anionenaustauschern festgehalten wird (mit Ausnahme von Methanol siehe Abbs. 1 und 4). An Hand von Säulenoperationen konnten diese Resultate bestätigt und dadurch unsere Annahme, dass das Thorium aus derartigen Lösungen tatsächlich als negativ geladener Chloridkomplex vom Harz adsorbiert wird, bekräftigt werden.

2. EXPERIMENTELLER TEIL

(a) *Lösungen und Reagenzien*

Die verwendete Thoriumchloridlösung wurde folgendermassen hergestellt: Eine genau gewogene Menge an formelreinem Thoriumnitrat p.a. wurde solange mit konz. Salzsäure zur Trockne eingedampft bis keine Nitrationen in der Lösung mehr anwesend waren. Der nach vorsichtigem Abdampfen der überschüssigen Salzsäure erhaltene Rückstand bestehend aus Thoriumtetrachlorid wurde in konz. Salzsäure (12 n) gelöst. Die resultierende Lösung wies einen auf gravimetrischen und spektrophotometrischen Wege ermittelten Thoriumgehalt von 5 mg Thorium/ml auf.

Als Harze wurden die bei 50°C getrockneten stark basischen Anionenaustauscher Dowex 1 und Amberlite IRA 400 (Cl^-; 50 bis 100 mesh) verwendet. Als Reagens zur spektrophotometrischen Bestimmung des Thoriums wurde eine 0·1 %ige wässrige Thoronollösung angewendet. Die verwendeten aliphatischen Alkohole (Methanol, Äthanol, n Propanol, Isopropanol, n Butanol, Isobutanol und ein Amylalkoholgemisch) stellten p.a. Reagenzien dar. Ebenso wurden alle benötigten Salzsäurelösungen aus konz. Salzsäure p.a. hergestellt.

(b) *Apparatives*

Zur quantitativen Bestimmung des Thoriums diente ein Beckmann Spektrophotometer, Modell B. Die Messungen wurden in 1 cm Küvetten bei einer Wellenlänge von 545 mμ unter Anwendung einer blauempfindlichen Photozelle durchgeführt.

Die Säulenoperationen wurden mit Säulen des von uns schon mehrmals beschriebenen Typs[8] unter Einhaltung der dort angegebenen Dimensionen durchgeführt.

(c) *Quantitative Bestimmung des Thoriums*

Der nach dem Abfiltrieren des Harzes erhaltenen Lösung bzw. dem Effluenten nach einer Säulenoperation wurde ein aliquoter Teil entnommen und auf dem Wasserbad zur Trockne eingedampft. Der Rückstand wurde dann in möglichst wenig konz. Salzsäure aufgenommen und zur Zerstörung der aus dem Harz herausgelösten organischen Substanzen einige Tropfen Perhydrol zugesetzt. Nach Ablauf von ca. 1 bis 2 Stunden wurde die Lösung solange erwärmt (mit Uhrglas bedeckt) bis die Hauptmenge des Perhydrols zerstört war. Anschliessend wurde die Lösung auf dem Wasserbad zur Trockne eingedampft, der Rückstand mit insgesamt 40 ml 0·1 n Salzsäure in einen 50 ml Messkolben gebracht, dieser Lösung 5 ml der 0·1 %igen wässrigen Thoronollösung zugesetzt und mit 0·1 n Salzsäure auf die Marke aufgefüllt. Anschliessend wurde die Extinktion der Lösung gegenüber einen auf analoge Weise bereiteten Leerwert gemessen (siehe b). Der Thoriumgehalt der Messlösung konnte dann mittels einer Eichkurve sofort ermittelt werden. Im Falle geringer Thoriummengen wurden 10 ml Messkolben verwendet.

(d) *Ermittlung der Adsorbierbarkeit (Verteilungskoeffizienten)*

Das Gesamtvolumen betrug jeweils 25 ml. In jedem Falle enthielt die Mischung 5 mg Thorium d.h. 1 ml der Thoriumlösung. Der Prozentgehalt an Alkohol war 99, 96, 90 usw. bis 0 Prozent Alkohol. Bei Anwendung von 99 Prozent Alkohol wurde 1 ml der Thoriumlösung in einen Erlenmeyerkolben (mit Schliffverschluss) auf dem Wasserbad zur Trockne eingedampft, der Rückstand in 0·25 ml konz. Salzsäure gelöst und 24·75 ml des Alkohols zugesetzt. In allen anderen Fällen betrug die zugesetzte Menge an konz. Salzsäure entweder 1 ml oder mehr.

[8] J. KORKISCH, A. FARAG und F. MECHT, *Mikrochim. Acta* 415 (1958).

Vol. 15 1960

Hierauf wurde 1 g des Harzes (Amberlite IRA 400; Chloridform) zugesetzt und der gut verschlossene Kolben 24 Stunden lang auf einer Schüttelmaschine gut durchgeschüttelt. Anschliessend wurde vom Harz abfiltriert und wie unter c) beschrieben weiter verfahren. Auf analoge Weise nur

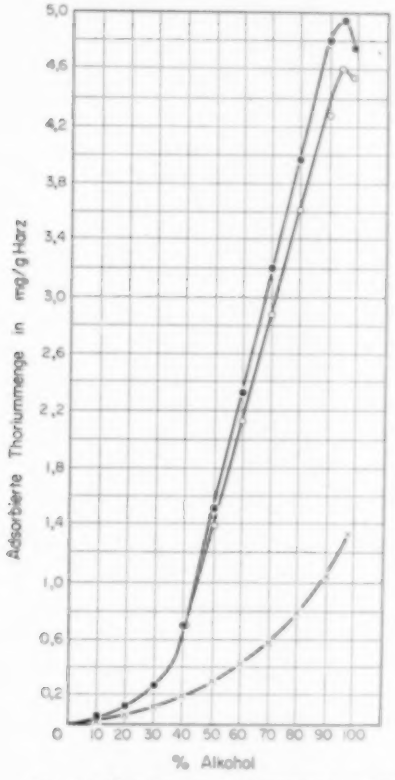

Abb. 1.—● n-Propanol, Isopropanol, n-Butanol, Isobutanol und Amylalkohol.
○ Äthanol.
× Methanol.

unter Anwendung von verschiedenen Thoriummengen wurde die bei Zimmertemperatur ermittelte Adsorptionsisotherme in 96 prozentigem Isopropanol und einer Gesamtacidität von 0·48 n an Salzsäure aufgestellt (siehe Abb. 3).

(c) *Säulenoperationen*

Nach der Vorbehandlung der Säule (Dowex 1; Chloridform) mit 50 ml einer Mischung bestehend aus 4 ml konz. Salzsäure und 96 ml Isopropanol wurde durch diese eine Lösung folgender Zusammensetzung fliessen gelassen: 0·5 ml der Thoriumlösung (2·5 mg Thorium) + 3·5 ml konz. Salzsäure + 96 ml Isopropanol. Die Fliessgeschwindigkeit betrug 0·5 ml/min. Der gesamte Effluent wurde eingedampft und wie unter c) beschrieben auf Thorium untersucht. Dieser enthielt keine Spur an Thorium d.h. die Gesamtmenge des Thoriums wurde am Harz festgehalten. Hierauf wurde das Harz mit 100 ml einer Lösung die analog der zur Vorbehandlung des Harzes verwendeten zusammengesetzt war, gewaschen. Der Effluent der Waschlösung enthielt ebenfalls kein Thorium. Die Acidität aller der hiebei verwendeten Lösungen war 0·48 n an Salzsäure. Analoge mit geringeren Thoriummengen (1000 bis 500 μg Thorium) durchgeführte Versuche ergaben, dass auch indiesen Fällen das Thorium quantitativ von Harz adsorbiert wurde. Durch Behandlung des Harzes mit

wässriger 0·1 n Salzsäure konnte alles Thorium wieder quantitativ eluiert werden. Analoge Versuche mit Amberlite IRA 400 (Chloridform) ergaben dasselbe Resultat. Abschliessend kann gesagt werden, dass unter den von uns gewählten Versuchsbedingungen eine quantitative Anreicherung des Thoriums aus salzsauren alkoholischen Lösungen an stark basischen Anionenaustauschern möglich ist.

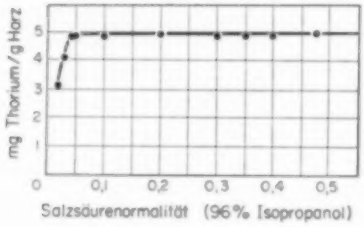

ABB. 2.

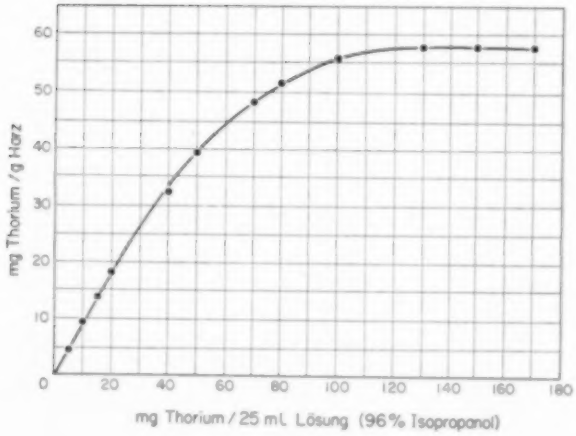

ABB. 3.

3. RESULTATE

In Abb. 1 wird der Einfluss der Alkoholkonzentration auf die Menge des am Harz adsorbierten Thoriums gezeigt. Wie daraus ersichtlich ist, nimmt die Menge des am Harz adsorbierten Thoriums mit steigender Alkoholkonzentration zu, erreicht ein Maximum bei 96 Prozent Alkohol und fällt dann etwas ab.

In der folgenden Abb. 2 wird der Einfluss der Acidität bei einer Alkoholkonzentration (Isopropanol) von 96 Prozent gezeigt. Daraus geht hervor, dass der Einfluss der Acidität nur sehr gering ist d.h. dass die am Harz adsorbierte Thoriummenge bis zum Beginn der Hydrolyse des Thoriumchlorids bei einer Acidität von 0·04 n Salzsäure praktisch konstant bleibt.

Abb. 3 zeigt den Verlauf der bei Zimmertemperatur in 96 prozentigem Isopropanol und bei einer Gesamtacidität von 0·48 n an Salzsäure ermittelten Adsorptionsisotherme. Daraus geht hervor, dass diese im Konzentrationsbereich von 0 bis 20 mg Thorium linear verläuft und die am Harz adsorbierte Thoriummenge ab einer Konzentration von 130 mg Thorium/25 ml Lösung praktisch konstant bleibt. Die hier adsorbierte Menge beträgt 58 mg Th/g Harz bzw. 1 mval/g.

Vol. 15 1960

In Abb. 4 wurden die Verteilungskoeffizienten des Thoriums gegen die Konzentrationen der verwendeten Alkohole aufgetragen. Der Verteilungskoeffizient ist gegeben durch:

$$K_d = \frac{\mu g \text{ Thorium/g Harz}}{\mu g \text{ Thorium/ml Lösung}}$$

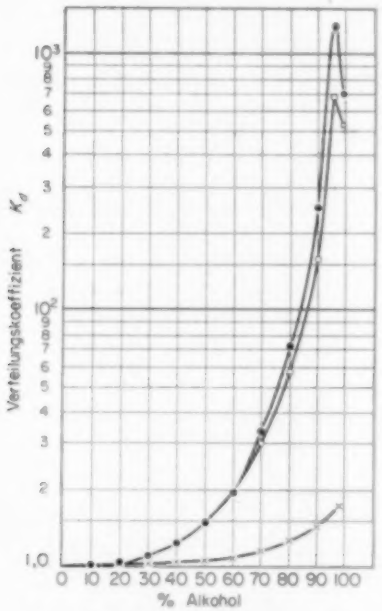

Abb. 4.—● n-Propanol, Isopropanol, n-Butanol, Isobutanol und Amylalkohol.
○ Äthanol.
× Methanol.

Diese Abbildung zeigt, dass die Verteilungskoeffizienten wie erwartet mit ansteigender Alkoholkonzentration zunehmen und bei hohen Konzentrationen sehr hohe Werte erreichen. Es ist also möglich das Thorium aus alkoholhaltigen salzsauren Lösungen an stark basischen Anionenaustauschern wie z.B. Dowex-1 oder Amberlite IRA-400 zu adsorbieren und zwar nach Durchführung einer Säulenoperation quantitativ, bei Anwendung der Gleichgewichtsmethode zu einen sehr hohen Prozentsatz wobei die Verteilungskoeffizienten besonders in sehr konzentriert alkoholischen Lösungen sehr hohe Werte annehmen. Im Gegensatz dazu, ist eine Anreicherung des Thoriums aus rein wässrigen salzsauren Lösungen an derartigen Harzen nicht möglich.[5,6]

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NOTES

Anomalous acceptor behaviour of boron tri-iodide

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In an examination of BI_3 chemistry, it was found that the iodide functions as a typical Lewis acid toward trimethylamine and N,N,-dimethylthioformamide in that 1:1 molecular complexes form. The complex from pyridine, however, had the composition $BI_3 \cdot 2C_5H_5N$ and did not have the properties of volatility and organic solubility associated with the molecular complexes. With the exception of $CHCl_3$ and CH_2Cl_2, the pyridine product was insoluble in non-polar solvents. Protonic solvents dissolved the product but decomposition occurred. The two pyridine molecules appear to be very tightly held since no loss of pyridine was observed at 150°/0·1 μ. An ebulliometric molecular weight determination in acetonitrile indicated, however, that this "complex" undergoes some type of dissociation (312 vs. theory of 550). All of these properties can be rationalized in the salt structure proposed below:

Excess boron iodide did not appear to convert this salt to the tetra-iodoborate.[1] Independent experiments with $(CH_3)_4NI$ and BI_3 gave no good evidence for tetra-iodoborate formation.

Further support for the salt structure was found in the reaction of the "complex" with iodine where 1 mole of iodine was absorbed to form what appeared to be the tri-iodide salt:

$$(C_5H_5N)_2BI_2^+I^- + I_2 \xrightarrow{CHCl_3} (C_5H_5N)_2BI_2^+I_3^-$$

A solution of this salt in CH_3CN showed the U.V. absorption band of I_3^-.

Triphenylphosphine, acetonitrile, and N, N-dimethylformamide also initially yielded "complexes" of unusual stoicheiometry: $BI_3 \cdot 3P(C_6H_5)_3$, $BI_3 \cdot 2CH_3CN$ and $BI_3 \cdot 4HCON(CH_3)_2$. Efforts to purify the nitrile and amide complexes were unsuccessful but the phosphine "complex" on recrystallization from hot chloroform lost triphenylphosphine and yielded a simple 1:1 molecular adduct. Extension of the pyridine reaction to silicon tetra-iodide yielded $SiI_4 \cdot 4C_5H_5N$ which could be formulated as $(C_5H_5N)_4SiI_2^{++}2I^-$. This compound also absorbed iodine.

Experimental

The complexes were prepared by mixing benzene solutions of BI_3 (or SiI_4) and the base; and those listed in Table 1 (p. 183), with the exception of the silicon compound, were recrystallized from chloroform. All complexes were decomposed by water as shown by the immediate precipitation of AgI on addition of $AgNO_3$. It should be noted that solutions of $(C_5H_5N)_2BI_2^+I^-$ and of $BI_3 \cdot 3P(C_6H_5)_3$ (crude) in chloroform were more highly conducting than chloroform itself; but the effect was not large enough to preclude the possibility of impurities.

Mr. A. F. Biddle of this laboratory indexed $BI_3 \cdot N(CH_3)_3$ as orthorhombic with $a_0 = 11{\cdot}94$ Å, $b_0 = 17{\cdot}00$ Å, $c_0 = 11{\cdot}35$ Å, and $z = 8$.

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[1] It has been suggested that $C_5H_5N \cdot BCl_3$ may have the structure $(C_5H_5N)_2BCl_2^+BCl_4^-$, however, we found that the ^{11}B magnetic resonance spectra of $C_5H_5NBCl_3$ and $C_5H_5NBBr_3$ in acetonitrile consist of single resonances in the region characteristic of simple BX_3 addition compounds.

Vol. 15 1960

1.5.60

TABLE 1.—BORON TRI-IODIDE COMPLEXES

Compound	B		I		C		H		N		m.p.	Colour
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.		
$BI_3 \cdot N(CH_3)_3$[a]	2·51	2·40	83·30	84·48	7·93	7·90	2·33	2·01	3·26	3·10	248–250°	Colourless
$BI_3 \cdot HCSN(CH_3)_2$	2·33	1·90	64·20	66·81	12·38	12·65	2·90	2·48	11·22 (S)	11·25 (S)	>250°	Yellow
$BI_3 \cdot P(C_6H_5)_3$[b]	1·63	1·65	57·18	58·23	33·84	33·06	2·56	2·31	4·96 (P)	4·74 (P)	>220° dec.	Ivory
$[BI_2(C_5H_5N)_2{}^+I^-]$	2·00	1·96	68·98	69·25	22·29	21·84	2·08	1·84	5·16	5·09	>220° dec.	Bright yellow
$[BI_2(C_5H_5N)_2{}^+I_3^-]$	—	—	78·61	78·97	14·38	14·95	1·63	1·25	—	—	—	Purple-brown
$SiI_4 \cdot 4C_5H_5N$	—	—	57·24	59·58	27·94	28·19	3·17	2·37	5·94	6·58	—	Ivory

[a] Molecular weight found (ethylene chloride): 444; theory, 450·66.
[b] Molecular weight found (ethylene chloride): 620; theory, 653·86.

The action of $NaBH_4$ on $NaHSO_3$

(*Received* 4 *January* 1960; *in revised form* 18 *March* 1960)

Sodium borohydride has been used in inorganic systems to reduce metal ions to lower valence states. It has also been shown to reduce some metal ions to black precipitates which analyse as borides. Oxidized halogen anions are reduced to halides. However, there are few other reports on the reduction of other anions.

In our work it was necessary to investigate the use of $NaBH_4$ in solutions containing sulphite ion. It was found that in highly alkaline, concentrated solutions the sulphite was reduced to sulphide. However, the addition of $NaBH_4$ to solutions of $NaHSO_3$ resulted in a different reaction. When the

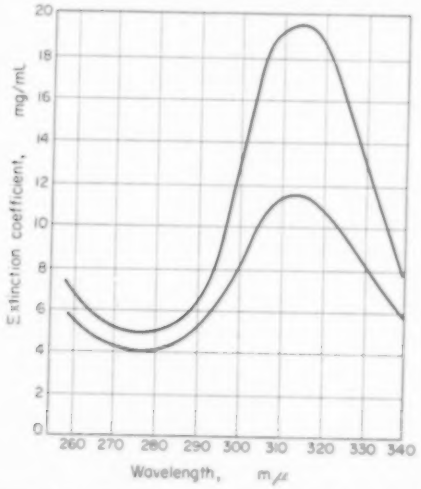

Fig. 1.—A comparison of the absorption spectra of sodium hydrosulphite (upper curve) and the sodium bisulphite–sodium borohydride reaction mixture (lower curve).

solution was made alkaline, it was found that it reduced anthraquinone to the red disodium salt of 9,10 dihydroxyanthracene. This action on anthraquinone did not take place if the bisulfite was made alkaline before the addition of the $NaBH_4$.

The reduction of anthraquinone to the red salt suggested the presence of hydrosulphite, one of the few reagents which can accomplish this reduction in aqueous solutions. The ultra-violet absorption spectrum of the bisulphite-borohydride solution was determined shortly after the mixture was made alkaline. The spectrum, shown in Fig. 1, is the same as that of hydrosulphite in alkaline solution. The extinction coefficients of both curves show a minimum at 280 mμ, and rise to a maximum at 315 mμ. Beyond this wavelength they decrease sharply. None of the other reactants or products have any measurable spectrum in this region in the concentrations used.

In a control experiment the $NaBH_4$ was added to the same weight of $NaHSO_3$ which had previously been made alkaline. There was no measurable ultra-violet spectrum.

While the shapes of the curves are identical, the numerical values of the extinction coefficients for the reaction mixture are in each case lower than those for pure hydrosulphite. This was expected. The $NaBH_4$ is very unstable at the acidity of the $NaHSO_3$. Furthermore, hydrosulphite is extremely unstable at this acidity so that some of it is destroyed as soon as it is formed. Even in alkaline solutions hydrosulphite is so unstable at high dilutions that transfers and dilutions must be made in the absence of oxygen.

Experimental

$NaHSO_3$ (100 mg) was dissolved in 75 ml of water, and 100 mg of $NaBH_4$ were added. After 1 min NaOH was added, and the solution diluted to 100 ml. The NaOH concentration was M/5 in the diluted solution.

Vol. 15 1960

In the control experiment the alkali was added before the $NaBH_4$.

The solutions were diluted for the spectrum determinations, which were conducted with a Beckmann DU Spectrophotometer. All transfers were made by syringe into deoxygenated water in vessels which had previously been flushed with argon. The same precautions were observed in the spectrum measurements on the known hydrosulphite.

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Preparation and crystal structure of americium metal*

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The crystal structure of americium has been studied using metal produced by two methods. The first method consisted of the reduction of approximately 20 mg quantities of americium trifluoride

Table 1.—Diffraction data for d.h.c.p. americium metal

hkl	$\sin^2\theta$		Intensity	
	calc.	obs.	calc.	obs.
10·0	0·0657	0·0663	11	trace
10·1	0·0704	0·0710	62	*m*
00·4	0·0752	0·0764	50	*s*
10·2	0·0845	0·0851	145	*vs*
10·3	0·1080	0·1079	36	*vw*
10·4	0·1408	—	8	—
10·5	0·1831	0·1841	16	*vvw*
11·0	0·1970	0·1973	38	*m*
10·6	0·2348	0·2353	33	*m*
20·0	0·2627	—	2	—
20·1	0·2674	—	9	—
11·4	0·2722	0·2727	45	*m*⁺
20·2	0·2815	0·2822	24	*vw*
10·7	0·2953	0·3000	7	*m*⁻
00·8	0·3006		7	
20·3	0·3050		7	
20·4	0·3378	—	2	—
10·8	0·3663	—	2	—
20·5	0·3801	—	5	—
20·6	0·4318	0·4327	12	trace
10·9	0·4462	0·4450	4	trace
21·0	0·4597	—	1	—
21·1	0·4644	—	7	—
21·2	0·4785	0·4798	21	*vw*⁺
20·7	0·4929	0·4972	4	*m*⁺
11·8	0·4976		18	
21·3	0·5020	—	7	—
21·4	0·5348	0·5349	2	*w*
10·10	0·5354		10	

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

with barium vapour at 1000°C in an all-tantalum double crucible system. The products were allowed to cool for 10–16 hr in vacuum, without controlled annealing. Spectrographic analysis of the resulting metal showed 2 wt.% of impurities which were barium (1·6%), calcium (0·1%), magnesium (0·1%), and aluminium (0·2%). In the second method americium dioxide, prepared by the decomposition of the oxalate in the air at 600°C, was reduced with lanthanum metal at 1200°C. The large difference in the volatility of americium and lanthanum metals enables the product to be separated by distillation.

TABLE 2.—DIFFRACTION DATA FOR VAPOURIZED AMERICIUM

Observed		Calculated							
		f.c.c.			h.c.p.			AmO	
I	$\sin^2\theta$	Σh^2	$\sin^2\theta$	I	hkl	$\sin^2\theta$	I	Σh^2	$\sin^2\theta$
s	0·0749	3	0·0746	50	00·2	0·0745	13		
diffuse	0·0840				10·1	0·0849	97		
vw									
mw	0·1002	4	0·0994	26					
vw	0·1885							8	0·1872
m	0·1995	8	0·1988	19	11·0	0·1988	19		
trace	0·2584							11	0·2574
ms	0·2742	11	0·2734	22	11·2	0·2733	23		
mw	0·3003	12	0·2982	6	00·4	0·2981	7		
vw	0·3987	16	0·3676	3					
mw	0·4726	19	0·4722	10					
m	0·4996	20	0·4970	9	11·4	0·4968	9		
mw	0·5967	24	0·5964	8	30·0	0·5963	4		
trace	0·6320							27	0·6318
m	0·6719	27	0·6710	3	30·2	0·6708	8		
					00·6	0·6707	3		
w	0·7939	32	0·7952	5	22·0	0·7950	5		
ms	0·8695	35	0·8698	23	22·2	0·8695	12		
					11·6	0·8694	12		
m	0·8948	36	0·8946	13	30·4	0·8943	13		
f.c.c.	A = 0·02485								
h.c.p.	A = 0·06625								
	C = 0·01863								
AmO	A = 0·0234								

The americium was effused through a 20 mil hole in the crucible cap and collected on a rotatable 10 mil dia. tantalum wire or quartz fibre located ≤ 2 mm above the effusion orifice. Twenty to one hundred microgrammes of americium, typically containing less than 0·5 wt.% of lanthanum were thus collected.

X-ray diffraction patterns were obtained using Cu Kα radiation and 90 mm and 114·6 mm dia. cameras. The powder patterns of the microcrystalline metal from the fluoride reductions have been indexed as double hexagonal close-packed with $a = 3{\cdot}474 \pm 0{\cdot}005$ Å and $c = 11{\cdot}25 \pm 0{\cdot}02$ Å. The relative intensities calculated from:

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

for the space group $P6_3/mmc$ with atomic positions: 2 Am in (0,0,0), (0,0,$\frac{1}{2}$), and 2 Am in ($\frac{1}{3}$,$\frac{1}{3}$,$\frac{1}{4}$), ($\frac{1}{3}$,$\frac{2}{3}$,$\frac{3}{4}$), are compatible with the visual estimates of the intensities of the powder pattern lines. The intensities and sine squares for all lines for which $I \neq 0$ and $\sin^2\theta < 0{\cdot}54$ are listed in Table 1. The proposed structure yields a calculated density of 13·61 $\pm$ 0·05 g/cm³ and a metallic radius of 1·73 Å.

Vol. 15 1960

The powder patterns from the metal produced by the vaporization technique can be interpreted in terms of small amounts of AmO (f.c.c., $a = 5{\cdot}05$)[1] and an intimate mixture of the cubic and hexagonal forms of close-packed atoms, resulting from faults in the stacking of the close-packed layers. This type of stacking fault has been treated by WILSON[2]. The hexagonal reflexions with $(h - k)/3$ = integral and l = even superimpose on the cubic reflexions and will be sharp. The remaining lines will be broadened because of the stacking faults. The above preparations were predominantly cubic, and the average f.c.c. unit cell constant on the basis of four preparations is $a = 4{\cdot}894 \pm 0{\cdot}005$ Å. The calculated density is $13{\cdot}65 \pm 0{\cdot}05$ g/cm³, and the metallic radius is 1·73 Å. The lines of a typical pattern are listed in Table 2.

After one of the vaporized samples, which had been indexed as f.c.c., was kept at dry ice temperature for a week, the pattern was predominantly hexagonal and agreed with the double hexagonal close-packed structure above. As the large scale reduction yields d.h.c.p. structure, and the f.c.c. phase goes to the d.h.c.p. phase on cooling, the d.h.c.p. phase is probably the α or room temperature form, and the f.c.c. phase becomes stable at a higher temperature.

GRAF *et al.* have reported a d.h.c.p. phase of americium with $a = 3{\cdot}642 \pm 0{\cdot}005$, $c = 11{\cdot}76 \pm 0{\cdot}01$ Å and metallic radius 1·82 Å,[3] but in the present work no metal with the larger cell dimensions has been obtained. It should be pointed out, however, that the results of GRAF and co-workers were reproduced in many successful reductions using both ^{241}Am and ^{243}Am, and that his metal appears to have been as pure as ours. It may be that americium, like cerium, exists in a "collapsed" as well as an expanded phase of the same structure type.

It must also be emphasized that spectrographic analysis is inadequate for the detection of all impurities, and particularly anionic impurities, small amounts of which may have an important effect on the structure.

Magnetic susceptibility measurements and high temperature X-ray studies are now in progress and will be reported in a future publication.

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The infra-red spectrum of $Th(OH)_4$

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$Th(OH)_4$ was precipitated from an aqueous solution of $Th(NO_3)_4$ with sodium hydroxide solution. The precipitate was filtered, washed several times with distilled water, then with ethyl alcohol and finally with dry distilled ether. It was then dried and powdered.

The infra-red spectrum of this $Th(OH)_4$ was measured on a Perkin–Elmer Model 21 infra-red spectrophotometer equipped with a NaCl prism. Both the KBr pressed-pellet technique and the Nujol mull technique were used, the former in the range 8–15 μ and the latter over the full range 2–15·5 μ. The results are given in Table 1, where a comparison is also made with some earlier work.[1]

The strong peak at 3295 cm^{-1}, not observed previously, is easily identified as an OH-stretch vibration. The peaks at 841 cm^{-1} and 1060 cm^{-1} are almost certainly fundamentals, and the new

peak at 1534 cm^{-1} may be a fundamental. It is probable that the weak peaks at 1299 cm^{-1} and 1406 cm^{-1} are combination frequencies.

A definite choice of symmetry is not yet possible. DUVAL and LECOMTE[1] considered only the point groups D_{4h}, C_{4h} and C_{4v}. For the point groups D_{4h} and C_{4h} we would expect 8 infra-red-active vibrations, while C_{4v} would require 9. DUVAL and LECOMTE were of the opinion that the symmetry D_{4h} or C_{4h} is most probable, since it would be hard to explain the few bands found in the spectrum on the basis of a pyramidal structure.

TABLE 1.—INFRA-RED SPECTRUM OF $Th(OH)_4$

Wave numbers in KBr-pellet (cm^{-1})	Intensity	Wave numbers in mull (cm^{-1})	Intensity	Earlier values[1] (cm^{-1})
838	*m*	845	*s*	840
1059	*vs*	1061	*vs*	1045
—	—	1299	*vw*	1294
—	—	1406	*mw*	1438
—	—	1534	*m*	—
—	—	3295	*vs*	—

However, since the X—O—H submolecule is usually not linear, point groups such as T_d, D_{4h} or C_{4v} are not likely to be correct. C_4 is a possible point group, but DUVAL and LECOMTE's objection also applies to this symmetry. A final possibility is that the molecule possesses a distorted tetrahedral configuration.

It would consequently seem that C_{4h} is the most likely point group, but none of the other configurations mentioned above can with certainty be ruled out. A neutron diffraction study would probably be necessary to settle this point.

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Vol. 15 1960

Contributions to the solvent effect in the iodine–iodoantipyrine exchange reaction

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IN this investigation we have examined the effect of the solvent on the exchange rate and possible ways of accelerating the exchange reaction at constant temperature and concentration. The exchange between 1-phenyl-2,3-dimethyl-4-iodopyrazolone (4-iodo-antipyrine) and elementary iodine was chosen as a model reaction. The former is sufficiently soluble in most of the solvents and may readily be prepared and purified. The iodine is rather nucleophilic, and therefore it would be expected that, owing to dissociation to form I^+ ions, the exchange rate will increase in polar solvents.

Experimental

In the experiments iodo-antipyrine was labelled at a specific activity of about 2500–3000 cpm/mg. The concentration of the reactants was $7 \cdot 10^{-3}$ M. The reaction was quenched by adding arsenious acid, and iodide was precipitated with silver nitrate acidified with perchloric acid. AgI was centrifuged,

washed, filtered, and its weight and activity were measured. By plotting values of log $1-(x_t)/(x_\infty)$ against time, the half-time of exchange $t_{1/2}$ was found. The specific activity at infinite time $\sqrt{(x_\infty)}$ was found from the exchange in a 50 per cent aqueous ethanolic solution, in which $t_{1/2} \cong 10$ sec. No zero-time exchange was observed.

Results

The effect of the dielectric constant was examined at 21°C (Table 1).

TABLE 1

Solvent	ε_0	$t_{1/2}$
Dioxane	3·0	55 min
Chloroform	5·1	43 min
Pentanol	16·0	160 min
Ethanol	25·8	40 min
Nitrobenzene	35·5	<20 sec
Formamide	>84	~10–15 min

$t_{1/2} \cong 1$ min in water at reactant concentrations of $2 \cdot 10^{-3}$ M.

It appears from the above data that the rate of exchange is not only dependent on ε; presumably the structure of the solvent, as manifested in the viscosity and in steric factors, plays an appreciable role. It is difficult to study the solvent effect systematically because of the difficulty of varying only one of the properties (e.g. ε).

However, a monotonic change can be expected within a homologous series, and for this purpose the exchange reaction was examined in various alcohols at 21°C (Table 2).

TABLE 2

Solvent	$t_{1/2}$
CH_3OH	6·5 min
C_2H_5OH	40 min
n-C_3H_7OH	95 min
n-C_4H_9OH	111 min
$C_5H_{11}OH$	160 min

The rate of exchange is affected by the water content of the solvent to an appreciable extent (Table 3)

TABLE 3

Solvent	$t_{1/2}$ (19°C)
C_2H_5OH	40 min
C_2H_5OH + 6 vol. % H_2O	15 min
n-C_3H_7OH	95 min
n-C_3H_7OH + 4 vol. % H_2O	45 min
Dioxane	55 min
Dioxane + 10 vol. % H_2O	7·5 min

These results suggest that by means of a suitable calibration curve it may be possible to calculate the water content from the value of $t_{1/2}$. It may be possible to generalize this principle to measure the concentration of one solvent which accelerates exchange in another solvent where exchange is slow. The fields of application might be extended by using other exchange reactions. Further investigations in this direction are in progress.

The solvent effect was also investigated in the case of aromatic compounds (Table 4).

TABLE 4

Solvent	$t_{1/2}$ (19°C)
Benzene	35 min
Toluene	26 min
Chlorobenzene	9 min
Nitrobenzene	<20 sec

The various substituents do not show unequivocal effects, as the reaction is accelerated both by the nucleophilic $-CH_3$ group and by the electrophilic $-Cl$. In nitrobenzene I^+ is probably formed and thus the exchange is very rapid. To clarify this problem the exchange reaction will be studied in other aromatic solvents.

The exchange reaction was also carried out in the presence of compounds which promote the heterolytic dissociation of iodine, e.g. $HgCl_2$, $AgNO_3$. These experiments were conducted in an ethanolic medium at 21°C (Table 5).

TABLE 5

Solvent	$t_{1/2}$
Ethanol	40 min
Ethanol + $HgCl_2$	<1 min
Ethanol + $AgNO_3$	<10 sec

The overall reaction between Ag^+ and I_2 may be written:

$$6Ag^+ + 3I_2 + 3H_2O = 5AgI + AgIO_3 + 6H^+.$$

The first step, viz. $Ag^+ + I_2 = AgI + I^+$, is followed by rapid disproportionation of the I^+ ions:

$$3I^+ + 3H_2O = 2I^- + IO_3^- + 6H^+,$$

but the exchange between I^+ ions and iodo-antipyrine is more rapid than the disproportionation. No exchange was found between IO_3^- and iodo-antipyrine, and the exchange between I^- and iodo-antipyrine is extremely slow ($t_{1/2} \simeq 2$ days).

The results show the important role of I^+ ions in the exchange reaction. As the I atom of iodo-antipyrine exchanges instantaneously with I^+ ion, it is possible to demonstrate in this way the intermediate formation of I^+ ions in certain chemical reactions.

The temperature and concentration dependence of the exchange reaction will be discussed at a later date.

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Vol. 15 1960

Interconversion of boranes—III. An analysis of the "first stable intermediate" problem

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WHEN diborane is heated to temperatures near 100°C thermal decomposition to produce many of the higher boron hydrides proceeds at a convenient rate. The mechanism of this decomposition reaction

has received considerable attention.[1,2] Some of the reactions occurring may be regarded as relatively well established and a few of the details of the reaction mechanism are generally accepted. Thus, to fit the observed kinetics of the decomposition, both CLARKE and PEASE and BRAGG and co-workers postulate a rapid dissociation of diborane to BH_3 groups followed by reaction of the BH_3 group with a diborane molecule in the rate-limiting step of the reaction. No borane containing three boron atoms has ever been isolated and the unstable intermediate postulated by both groups is rapidly converted to more stable boron hydrides. The predominant higher boron hydride formed is pentaborane-11 and little doubt seems to exist concerning this point. Thus the careful studies of BRAGG and co-workers following the reaction with the mass spectrometer have been recently confirmed by STEWART and ADLER who separated and identified the products by conventional vacuum line methods.[4]

Both some of the workers referred to above and others who have reviewed the decomposition reactions[5] have tended to write mechanisms showing pentaborane-11 as the first stable higher borane formed from the unstable triborane. CLARKE and PEASE, however, suggested that tetraborane-10 was first formed. It should be mentioned also that BRAGG and co-workers expressed the feeling that tetraborane-10 is somehow involved in the early stages of the reaction and LIPSCOMB mentions that the reaction

$$B_3H_7 + B_2H_6 \rightarrow B_5H_{11} + H_2 \qquad (1)$$

may not occur in a single step.[5] The purpose of this paper is to examine the information available at the present time to see if it permits decision as to whether pentaborane-11 is produced directly from the triborane intermediate with subsequent conversion of a portion of it to the small amounts of tetraborane-10 actually observed or whether it is obtained by prior formation and subsequent rapid conversion of tetraborane-10.

It is our belief that tetraborane-10 is in fact the first stable boron hydride produced by decomposition of diborane but is too reactive to isolate as a major product in the experiments thus far described. To establish this point it is necessary to demonstrate the validity of three points: (1) Under the usual conditions of the pyrolysis experiment the thermodynamically stable product is pentaborane-11. (2) Under the usual conditions of the pyrolysis experiment the kinetics of conversion of tetraborane-10 to pentaborane-11 are sufficiently rapid so that little more than steady state concentrations of the former would be observed. (3) Evidence exists that under conditions suitable for its isolation tetraborane-10 is in fact isolated from the pyrolysis products in good yield and that this isolation is possible because of kinetic and not thermodynamic factors.

Considerable information has been accumulated concerning the first factor. Thus BURG and SCHLESINGER showed that the reaction

$$2B_4H_{10} + B_2H_6 \rightarrow 2B_5H_{11} + H_2 \qquad (2)$$

is nearly an equilibrium.[6] STEWART and ADLER[4] reported a preliminary determination of the equilibrium constant for this reaction at 112°C as about 10^9 mm^{-1}. Thus, in a typical pyrolysis reaction in which near the outset the partial pressures of diborane, hydrogen, and pentaborane-11 might be 100 mm, 10 mm and 10 mm respectively, the tetraborane-10 pressure would be of the order of magnitude of 0·3 mm. In other words, the equilibrium mixture under these conditions would contain more than 30 times as much pentaborane-11 as tetraborane-10. Thus, in itself the confirmed observation of major pentaborane-11 formation is thermodynamically proper and may or may not arise from a kinetic cause.

Study of the rate of reaction (2) in the forward direction has been carried out by two different groups of workers.[7,8] Reaction (2) was found to be too rapid to measure at 100°C and above.

[1] R. P. CLARKE and R. N. PEASE, *J. Amer. Chem. Soc.* **73**, 2132 (1951).
[2] J. K. BRAGG, L. V. MCCARTY and F. J. NORTON, *J. Amer. Chem. Soc.* **73**, 2134 (1951).
[3] R. E. ENRIONE and R. SCHAEFFER, *J. Inorg. Nucl. Chem.* In press (1960).
[4] R. D. STEWART and R. G. ADLER, Abstracts of Papers Presented at the 134th American Chemical Society Meeting, p. 6S, Chicago, 1958.
[5] See for example W. N. LIPSCOMB in *Advances in Inorganic Chemistry and Radiochemistry* Vol. I, p. 149. Academic Press, New York (1959).
[6] A. B. BURG and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **55**, 4009 (1933).
[7] J. DUPONT and R. SCHAEFFER, *J. Inorg. Nucl. Chem.* **15**, In press (1960).
[8] R. K. PEARSON and L. J. EDWARDS, Abstracts of Papers presented at the 132nd American Chemical Society Meeting, p. 15N, New York (1957).

Calculation of the first order rate constants from the equation given in reference (7) gives an approximate value of the rate constant at 112°C of 1·26 min^{-1}. The time for conversion of half of any sample of tetraborane-10 to pentaborane-11 at this temperature is calculated to be slightly over 30 sec. It may therefore be concluded that data related to total product analysis in the direct studies of the pyrolysis quoted above cannot allow conclusive choice between tetraborane-10 and pentaborane-11 as the first stable boron hydride produced since both thermodynamics and kinetics require the latter to be the major component. To obtain a satisfactory answer to this question requires that one turn to experiments of a different type.

KLEIN *et al.* described in 1958 a convenient method for the preparation of tetraborane-10 and pentaborane-11.[9] At the time the work of KLEIN *et al.* was reported the work of STEWART and ADLER was unavailable and no inferences were drawn concerning the mechanism of conversion of diborane to higher boron hydrides. Nevertheless, an apparently intimate relation exists and these experiments deserve further attention in light of the arguments made above. Basically the work described by KLEIN *et al.* concerns the decomposition of diborane in a hot-cold tube reactor consisting of two concentric test tubes connected by a Dewar seal at the top. The outside of the reactor was kept at −78°C whereas the inside was heated to 120°C. In some respects this system is ideally suited to observe which higher hydride is first formed since both tetraborane-10 and pentaborane-11 are substantially completely removed from the reaction system once the products of the gas phase pyrolysis diffuse to the cold wall and are condensed to the liquid. The probability that subsequent reaction might occur in the liquid phase at −78°C seems very small. Previous studies have shown the decomposition of diborane occurs largely in the vapour phase and is not markedly affected by surface. Furthermore, KLEIN *et al.* concluded that in their reactor reaction is taking place at least to a large extent in the vapour phase. Under these conditions tetraborane-10 was by far the most important product. Only tetraborane-10 and pentaborane-11 appear to be produced and the former exceeded the latter by factors of 4·4 to 26 depending upon the exact nature of the reactor and the time of heating.

In themselves, these experiments, striking as they appear, are insufficient to settle the question of interest here. Thus it could easily be argued that pentaborane-11 was in fact the first product and was converted in large measure back to the tetraborane-10 by equilibrium (2). However, this position is untenable in light of the subsequent measurements of the equilibrium constant by STEWART and ADLER.

It cannot be stated that the problem of the "first stable intermediate" is completely resolved by the above line of argument. Further direct experimental confirmation would be desirable but additional simple tests are not obvious.

A further corollary of the above conclusions warrants specific attention. ENRIONE and SCHAEFFER have recently advanced support for the hypothesis that the rate controlling step in the decomposition of diborane is the elimination of hydrogen from the B_2H_6 molecule to form a reactive B_2H_7 intermediate. If this hypothesis is in fact true, and further verification of it would also be desirable, the line of argument presented in this paper suggests that the fate of the B_2H_7 molecule in the presence of diborane is the formation of tetraborane-10 by the reaction which might best be written

$$B_2H_7 + B_2H_6 \rightarrow B_4H_{10} + BH_3 \qquad (3)$$

Reactions of tetraborane-10, such as that illustrated by equation (2), hence appear unlikely to occur by cleavage to B_2H_7 and subsequent conversion of it to pentaborane-11. No argument presented here can be regarded as excluding the possibility that the reactive triborane intermediate reacts by two or more pathways with simultaneous formation of more than a single product. If such branching occurs, however, the evidence given above strongly suggests that only relatively minor amounts of the intermediate are converted directly to products other than tetraborane-10. Even minor conversion of B_2H_7 directly to pentaborane-11 could allow reaction (2) to proceed by this pathway if the cleavage to the triborane were reversible. Consequently additional experimental evidence is required on this point and will be presented in a forthcoming publication.[10]

[9] M. J. KLEIN, B. C. HARRISON and I. J. SOLOMON, *J. Amer. Chem. Soc.* **80**, 4149 (1958).
[10] See the Ph.D. Thesis submitted by GERALD BRENNAN to Iowa State University in May, 1960.

Vol. 15 1960

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A correlation between the degree of ionization of phosphates and the frequency of phosphorus magnetic resonance

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ORTHO-PHOSPHORIC acid is used widely as a standard for phosphorus nuclear magnetic resonance spectra. For it to be used as an internal standard in aqueous solutions a knowledge of the variation

TABLE 1

	Literature[a]		Present work	
	M = Na	M = K	M = Na	M = K
	(p.p.m. with respect to orthophosphoric acid)			
MH_2PO_4	0 ± 1, $+1{\cdot}3$[b]	-1 ± 1	$-0{\cdot}5 \pm 0{\cdot}1$	$-0{\cdot}4 \pm 0{\cdot}1$
M_2HPO_4	$+3 \pm 1$	-1 ± 1	$-3{\cdot}5 \pm 0{\cdot}1$	$-3{\cdot}4 \pm 0{\cdot}1$
M_3PO_4	-5 ± 1	-6 ± 1	$-6{\cdot}0 \pm 0{\cdot}1$	$-5{\cdot}8 \pm 0{\cdot}1$

[a] From ref. 1. except where indicated.
[b] From ref. 2.

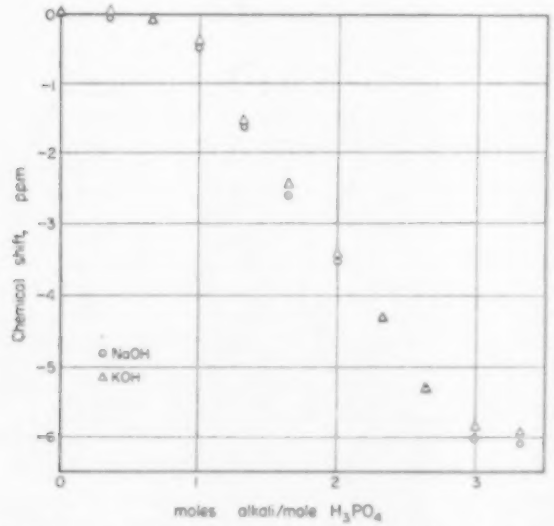

FIG. 1.—Variation of chemical shift (in parts per million relative to orthophosphoric acid) with ionization as $H_3PO_4 \rightarrow PO_4^{\equiv}$.

of the resonance peak with the degree of ionization is needed. It is not clear whether shielding of the phosphorus in the species H_3PO_4, $H_2PO_4^-$, HPO_4^{--}, and PO_4^{---} would increase with the ionization (because of the increasing charge) or decrease (because of distribution of the same number of electrons over a larger volume as a consequence of expansion). However, at least a smooth curve would be expected, which should be identical for sodium and potassium salts. The peaks found from mixtures of two of the species should also fall on the curve as exchange would be rapid. These conclusions were not borne out by the rather rough measurements reported in the literature[1,2] but reinvestigation (see Table 1 and Fig. 1) showed that the earlier work had been partly in error and that the shift of the resonance peak decreased smoothly as $H_2PO_4^- \rightarrow PO_4^{---}$.

There is evidence that phosphoric acid is ionized to form $H_4PO_4^+$ in sulphuric acid,[3] and we found that the frequency of the resonance peak decreases as the H_0 of sulphuric acid solutions of phosphoric acid became more negative; thus, as $H_0 = -2{\cdot}2$, 5·0, 8·6 we found $\sigma = -0{\cdot}3$, $-1{\cdot}0$, $-2{\cdot}5$.

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[1] J. R. van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *J. Amer. Chem. Soc.* **78**, 5715 (1956).
[2] N. Muller, P. C. Lauterbur and J. Goldenson, *J. Amer. Chem. Soc.* **78**, 3557 (1956).
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The half-life of ^{181}Hf *

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The half-life of ^{181}Hf has been variously reported[1,2,3] to be about 45 days. These determinations were made by following the decay of thermal-neutron-irradiated hafnium by gross counting of both gamma and beta radiation. Since the formation of the 70 day ^{175}Hf under these conditions is reported[4] to be comparable to that of ^{181}Hf, the gross decay curve exhibited by a sample thus irradiated should exhibit curvature, the exact nature of the curve depending upon the sensitivity of the particular detector for the individual radiations. The reported half-life of 45 days might therefore be too long for ^{181}Hf. We have attempted to minimize the effect of ^{175}Hf by production methods and discriminate counting techniques.

Activated hafnium sources were produced by the (n, γ) reaction on natural hafnium with degraded fission-spectrum neutrons. The relatively small number of thermal and epithermal neutrons increased the ratio ^{181}Hf to ^{175}Hf. The activities of these sources were followed on both a methane-flow type end-window proportional counter sensitive to particulate radiations, and on a sodium iodide gamma scintillation crystal, shielded from β-radiation with 200 mg/cm² of Be. Independent experiments on samples which contained only ^{175}Hf (produced by $^{176}Hf(n, 2n)^{175}Hf$ with 14 MeV neutrons from a Cockcroft–Walton accelerator) showed the proportional counter efficiency for ^{175}Hf to be only about

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

[1] J. M. Cork, A. E. Stoddard, W. C. Rutledge, C. E. Branyan and J. LeBlanc, *Phys. Rev.* **78**, 299 (1950).
[2] H. W. Wright, E. I. Wyatt, S. A. Reynolds, W. S. Lyon and T. H. Handley, *Nucl. Sci. Engng.* **2**, 427 (1957).
[3] H. S. Murdoch, *Proc. Phys. Soc.* A **66**, 944 (1953).
[4] *General Electric Chart of the Nuclides* (5th Ed.).

Vol. 15 1960

one-tenth that of the scintillator. Samples subsequently shown to contain almost entirely ^{181}Hf, on the other hand, were detected with comparable efficiencies on both counters. Decay was followed for approximately ten months, by which time counting statistics became rather poor. Both types of counters were constantly checked for performance with standard uranium sources. Visual examination of the curves of the logarithm of the decay rate versus time yielded only a single component with half-life between 42·5 and 43·5 days.

The counting data were then analysed for a single-component half-life by a least-squares reiterative calculation on an IBM 704 computer. The code required the half-life to change by less than 10^{-6} days between iterations before the calculation was allowed to end. Table 1 lists the results:

TABLE 1.—HALF-LIFE DETERMINATIONS OF ^{181}Hf

Sample	Irradiation number	Proportional counter	NaI scintillation counter
1	1	42·42 days	42·52 days
2	1	42·45	43·32
3	1		43·16
4	1		42·89
5	2	42·50	43·05
6	3		43·00
7	3		43·81
Average ± RMSD		42·45 ± 0·08 days	43·11 ± 0·37 days

While a small amount of ^{178}Hf in the samples would not have been detected by the proportional counter, it could have influenced the half-life measured by scintillation counting. Accordingly the scintillation counting data were analysed on the computer assuming a two-component decay with half-lives of 42·45 and 70 days. Good agreement was obtained for the ^{181}Hf/^{178}Hf ratios between samples from the same irradiation, with values of 27 and 40 for irradiations 1 and 3 respectively.

Since the slightly longer half-life obtained by scintillation counting is consistent with about 3% ^{178}Hf, and since the proportional counter is insensitive to this contaminant, we feel that the correct half-life for ^{181}Hf is 42·45 ± 0·08 days.

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Preparation of long-lived holmium-163*

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PREVIOUS investigations of holmium-163 have only indicated the presence of an activity with a 0·8 sec decay period.[1,2] This activity may be presumed to be an isomer of a long-lived ground state for which half-life limits have been set.[3] Holmium-163 is anticipated to have a ground-state nuclear spin of 7/2 and odd (negative) parity as is suggested from nuclear spectroscopic investigations of the other holmium isotopes. Similar considerations reinforce the measured value of 5/2 for the ground-state nuclear spin of stable dysprosium-163 and indicate odd (negative) parity.[4] However, an examination of the vicinal stable isotopes of odd atomic number indicates that holmium-163 is almost beta-stable. Thus, an allowed low-energy electron-capture decay of holmium-163 to dysprosium-163,

* Work done under the auspices of the U.S. Atomic Energy Commission.

[1] C. L. HAMMER and M. G. STEWART, *Phys. Rev.* **106**, 1001 (1957).
[2] N. B. GOVE, L. T. DILLMAN, R. W. HENRY and R. A. BECKER, *Bull. Amer. Phys. Soc.* (*Ser. II*) **2**, 341 (1957).
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probably accounts for the absence of holmium-163 in nature, although holmium-163 may be anticipated to have a long lifetime.

A sample of holmium-163 has been prepared by pile neutron irradiation of a sample of erbium oxide electromagnetically enriched one-hundredfold in the mass-162 isotope. Five milligrams of the erbium-162 sample contained in a quartz ampoule received an exposure of 2×10^{21} neutrons/cm^2 in the Materials Testing Reactor over a 3 month interval. Four months after the end of irradiation mass analysis of the sample (before chemical separation) in a 30 cm radius single direction focusing mass spectrometer showed the presence of isotopes of mass number 163 and 165 which were not observed

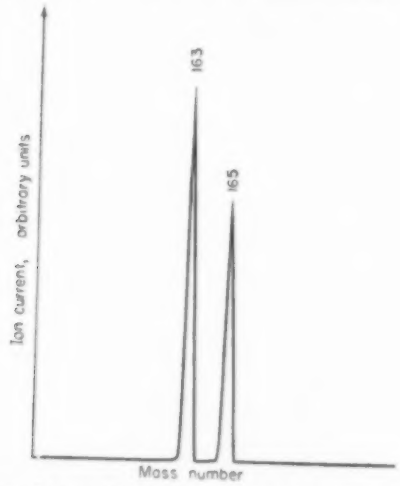

FIG. 1.—Mass spectrum of the purified holmium fraction showing the long-lived 163 and stable 165 holmium isotopes.

in the sample prior to irradiation. On the basis of the mass analysis, approximately 5–10 per cent of each of the erbium-162 and erbium-164 isotopes has undergone neutron capture.

The sample was next chemically fractionated by cation-exchange chromatography to yield pure fractions of the various rare earth elements. The thulium, dysprosium, and terbium fractions were identified by scintillation gamma spectroscopy which revealed the presence of thulium-170, dysprosium-159, and terbium-160. The erbium fraction was recognized by optical-emission spectroscopy, while weak gamma radiation extending to approximately 1 MeV (presumably due to holmium-166) characterized the holmium fraction. Mass spectrometric investigation of each fraction revealed the existence of isotopes at masses 163 and 165 in the holmium fraction (see Fig. 1); however no isotopes of these mass numbers were observed in either the erbium or dysprosium fractions in comparable yield. The erbium fraction did show considerable depletion of the erbium-167, which indicates the high capture cross section of this isotope.

From these data and the strength of the *K*-radiation in the holmium fraction (principally attributable to holmium-166), we conclude that the *K*-capture half life of holmium-163 is greater than 1000 years. The holmium fraction will be examined further for evidence of electron capture, and erbium-isotope capture cross-sections will be determined.

We should like to express our appreciation to the staff of the Materials Testing Reactor for carrying out the neutron irradiation.

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Vol. 15 1960

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LETTERS TO THE EDITOR

Dipyridine complexes of astatine salts

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THE tendency for the halogens to form negative ions decreases markedly with increasing atomic number, whereas the stability of positive ions increases. This trend suggests that astatine in particular should occur in a positive oxidation state.

The preparations of pyridine complexes of iodine in the uni-positive state are well known, and corresponding compounds have also been reported for bromine.[1] It was to be expected that similar complexes of astatine should show a marked stability. In the cases of the perchlorate and nitrate we have synthesised the astatine compounds, with iodine as a carrier, following in a general way the method described by CARLSON for the bromine compounds.

The astatine was obtained by irradiating Bi_2O_3 with 42 MeV He^{++} ions in the cyclotron, dissolving in nitric acid containing some iodine, separating bismuth as the phosphate, and extracting the astatine with chloroform.

For the perchlorate we used the silver dipyridine perchlorate, of which we dissolved 7·32 g in 15 ml chloroform and 1·5 ml pyridine. To this we added 30 ml chloroform containing astatine with a small amount of iodine carrier, and then 5·1 g of solid iodine. Under these conditions it is necessary to continue stirring until the reaction is finished, when the mixture changes colour from yellow to red. Silver iodide is separated from the liquid by centrifuging and filtering, and iodine dipyridine perchlorate carrying astatine is precipitated by the gradual addition of about 40 ml ether.

Iodine samples, as palladium iodide, PdI_2, were obtained from the solution of the complex before and after precipitation. (These solutions were reduced with sulphite before the addition of palladium nitrate and nitric acid.) The astatine concentration in the palladium iodide was measured by α-counting of infinitely thick samples. The astatine to iodine concentration ratio in the complex was about two to three times the average value before complex formation, indicating that astatine formed the complex preferentially. During a series of repeated recrystallizations by dissolving in chloroform and pyridine and adding ether, the astatine to iodine ratio decreased slowly without, however, falling to the original value.

The synthesis of the nitrate is somewhat more difficult. It is made as is the perchlorate, but in this case the pyridine silver complex cannot be isolated. Therefore, 2 g silver nitrate are dissolved in 3·3 ml pyridine and 5 ml chloroform; 30 ml chloroform containing astatine with some iodine carrier and 3 g iodine are added. From here the synthesis is performed as in the case of the perchlorate but the chloroform solution must be added slowly to the ether with energetic stirring. The complex nitrate is less stable than the complex perchlorate; the solid salt decomposes fairly rapidly with formation of iodine. In this case, too, the astatine to iodine ratio in the complex is found to be higher than the average value before complex formation.

That the astatine concentration is increased in the positive iodine fraction of the complex perchlorate and nitrate, relative to that in the original solution, is in agreement with the general behaviour of astatine as discussed in the beginning of this note.

Acknowledgements—This investigation was performed as part of the progamme of the Foundation for Fundamental Research of Matter (F.O.M.) with the financial support of the Organisation for Pure Research (Z.W.O.). Thanks are due to the cyclotron crew for numerous irradiations.

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[1] H. CARLSON, *Ber.* **68**, 2209, 2212 (1935).

Coprecipitation of astatine iodide with solid iodine

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It has been suggested that the extraction of astatine from an aqueous solution by an organic liquid—at least in the presence of iodine—takes place as AtI, a process analogous to the extraction of I_2.[1,2] To prove the existence of astatine iodide in solution in an organic medium, we have examined the coprecipitation of astatine with solid iodine from solutions in chloroform.

Astatine was prepared by α-bombardment of bismuth oxide. The irradiated material was dissolved in dilute perchloric acid and the bismuth precipitated as the phosphate and the astatine extracted into chloroform together with a small quantity of iodine added to the aqueous phase. Equal volumes of

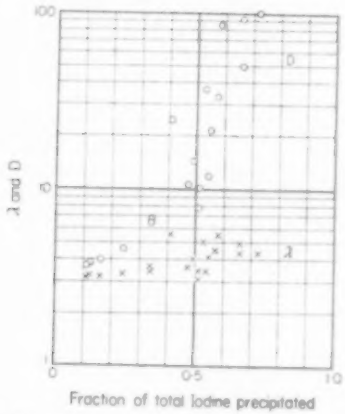

FIG. 1.—Each experiment is represented by one value of λ and one value of D. The average value of $\lambda = 4{\cdot}0$.

the chloroform solution are added to different quantities of solid iodine. The iodine is dissolved by heating on a water-bath. On cooling again in ice water, part of the iodine crystallizes out. The supernatant liquid is separated from the crystals and the iodine in each fraction extracted by, or dissolved in, a sulphite solution. The iodide is then precipitated with palladium nitrate and nitric acid and the activity determined in both fractions. We have used α-counting in all cases, which procedure determines only the ^{211}At. If one makes certain that all samples have the same composition and infinite thickness, then for constant geometry the counting rates are proportional to the specific activities. In each series of experiment the sum of the activities of the two fractions was the same for all parallel experiments, within limits comparable to the accuracy of the activity determination (~10% from the average). Half-lives were measured for all samples to exclude the possibility that an important fraction of the measured activity might be due to ^{210}Po. (It should be kept in mind that the α-beam of the Amsterdam cyclotron is contaminated with deuterons to a variable degree.)

The results of our most reliable set of measurements are given in Fig. 1. It is seen that the results are in reasonable agreement with formula (1), the logarithmic distribution law of DOERNER and HOSKINS[3], but not with (2), the homogeneous distribution law of Berthelot-Nernst.

$$\log \frac{\text{(astatine in solution)}}{\text{(astatine in solution + precipitate)}} = \lambda \log \frac{\text{(iodine in solution)}}{\text{(iodine in solution + precipitate)}} \qquad (1)$$

$$\frac{\text{(astatine in precipitate)}}{\text{(astatine in solution)}} = D \frac{\text{(iodine in precipitate)}}{\text{(iodine in solution)}} \qquad (2)$$

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[3] N. A. BONNER and M. KAHN in A. C. WAHL and N. A. BONNER, *Radioactivity Applied to Chemistry* pp. 106, 107. John Wiley, New York (1951).

Vol. 15 1960

(The symbols λ and D supposed to be constants, represent the logarithmic and the homogeneous distribution coefficients, the words astatine and iodine indicate the total quantity of each element in the various fractions.) The value of λ is about 4, the variations are in part due to inaccuracies in the activity measurements and in part to differences in the conditions of the experiments, to which differences the temperature at which the iodine crystals have formed is likely to have made an important contribution.

Similar results have been obtained in many earlier experiments in which the astatine was separated with silver iodide or with silver iodide plus silver.[1] This method, however, sometimes caused serious and unexpected losses of astatine, which were later avoided by the use of palladium iodide.

The reasonable validity of formula (1) and the high value of λ indicate that we are dealing with real coprecipitation rather than with an adsorption phenomenon. This conclusion strongly suggests that astatine is present in the chloroform solution as AtI, which should fit easily into the lattice of iodine molecules.

Acknowledgements—This investigation was performed as part of the programme of the Foundation for Fundamental Research on Matter (F.O.M.) with the financial support of the Organization for Pure Research (Z.W.O.). Thanks are due to the cyclotron crew for a large number of irradiations.

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[1] A. H. W. ATEN, JR., T. DOORGEEST, U. HOLLSTEIN and H. H. PH. MOEKEN, *Analyst* **77**, 774 (1954).

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60

Structure and electrical properties of some new rare earth arsenides, antimonides and tellurides

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A LITERATURE survey of the arsenides, antimonides and tellurides of the rare earth metals, scandium and yttrium, indicated that only a minor percentage of these compounds had been prepared. In an attempt to complete this list of compositions, we have prepared a series of *AB*-type compounds, where A = Sc, Y and rare earth metal; B = As, Sb, and Te. The lattice parameters of these compositions, together with those previously reported in the literature, are summarized in Table 1. While all reported arsenides and antimonides crystallize in the face-centred cubic NaCl structure, some tellurides crystallize in non-cubic structures. ScTe has a hexagonal structure; GdTe is monoclinic. For the LaTe which we prepared, we also found a monoclinic structure with the following parameters: $a_0 = 5{\cdot}554$, $b_0 = 7{\cdot}877$, $c_0 = 4{\cdot}103$, $\beta = 96\,0{\cdot}3'$. On the basis of a comparison of the X-ray powder patterns, it appears that PrTe, NdTe and SmTe are isomorphic with this structure. Whether the discrepancy between the structures found by us and the ones reported by IANDELLI[2] can be explained by polymorphic modifications or whether it is due to a deviation in stoichiometry would have to be established in a refined and more detailed investigation. The parameters of the non-cubic compounds were obtained from X-ray powder patterns and the given structures represent the best suggestion in concordance with the found and calculated d-spacings, since no single crystals were available.

In general, the compounds were prepared by direct synthesis from the elements, either in evacuated and sealed quartz ampules, or under purified argon atmosphere. All compounds had a grey metallic appearance and melted above 1000°C. Some electrical data are summarized in Table 2.

TABLE 1.—LATTICE PARAMETERS (IN Å UNITS) OF THE *AB*-TYPE RARE EARTH ARSENIDES, ANTIMONIDES AND TELLURIDES

Element *A* / *B*	As	Sb	Te
Sc	5·487	5·859	$a_0 = 6·728$ $c_0 = 8·360$
Y	5·786	6·163	6·095
La	6·125[1]	6·475[1]	6·409[2]
Ce	6·060[1]	6·399[1]	6·346[2]
Pr	5·997[1]	6·353[1]	6·309[2]
Nd	5·958[1]	6·309[1]	6·249[2]
Sm	5·921[3]	6·271[3]	6·594[3]
Eu	—	—	6·584[4]
Gd	5·854	6·217	$a_0 = 8·623$ $b_0 = 9·053$ $c_0 = 3·186$ $\beta = 91°1'$
Tb	5·813	6·178	6·101
Dy	5·780	6·153	6·092
Ho	5·759	6·129	6·072
Er	5·732	6·106	6·063
Tm	5·711	6·083	6·042
Yb	5·698	5·922	6·353[5]
Lu	—	—	—

TABLE 2.—ELECTRICAL RESISTIVITIES AND SEEBECK COEFFICIENTS OF THE REPORTED COMPOUNDS

	As		Sb		Te	
Element *A* / *B*	Resist (m Ω cm)	Seebeck coeff. (μV/°C)	Resist (m Ω cm)	Seebeck coeff. (μV/°C)	Resist (m Ω cm)	Seebeck coeff. (μV/°C)
Sc	$12·6 . 10^3$	−70	93	+50	$9·5 . 10^3$	−255
Y	220	+16	3·5	+14	$7·2 . 10^3$	−921
La	—	—	—	—	$4·7 . 10^3$	−834
Ce	—	—	—	—	—	—
Pr	—	—	0·08	+16	$0·38 . 10^3$	−52
Nd	—	—	0·16	+13	$6·3 . 10^3$	−170
Sm	14·9	+19	0·03	+6	$97·9 . 10^3$	−314
Eu	1·8	+25	35·9	+55	—	—
Gd	3·9	+9	0·19	+22	$4·8 . 10^3$	−240
Tb	1·8	+18	27·5	+10	15·0	−168
Dy	13·8	+12	69	+30	1·7	+15
Ho	4·0	+9	125·7	−40	0·28	+39
Er	7·2	+16	173·0	+60	0·20	+21
Tm	14·7	+7	26·4	−13	264	−700
Yb	128	+16	13·4	+6	$1·0 . 10^3$	−680
Lu	—	—	—	—	—	—

[1] A. IANDELLI, *Atti Acad. Nazl. Lincei* **25**, 498 (1937).
[2] A. IANDELLI, *Atti Acad. Nazl. Lincei* **85**, 881 (1955).
[3] A. IANDELLI, *Z. Anorg. Chem.* **288**, 81 (1956).
[4] W. KLEMM and H. SENFF, *Z. Anorg. Chem.* **241**, 259 (1939).
[5] W. KLEMM and H. SENFF, *Z. Anorg. Chem.* **242**, 92 (1939).

Vol. 15 1960

Most compositions exhibit a negative temperature coefficient of the electrical resistivity, indicating semiconducting behaviour.

L. H. Brixner

Contribution from the Pigments Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware

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J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 202 to 203. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

LOUIS GORDON, MURRELL L. SALUTSKY and HOBART H. WILLARD: **Precipitation from Homogeneous Solution.** John Wiley, New York, 1959. 187 pp., $7.50.

MORE than twenty years have passed since the advantages of precipitation from homogeneous solutions were called to the attention of analytical chemists. During this period, such precipitation techniques have found a host of applications in widely divergent fields.

The appearance, therefore, of a work devoted exclusively to a scholarly discussion of precipitation from homogeneous solution with respect to theories involved, specific techniques employed, intercomparison of results and theory, analytical applications and proposed research applications is of importance not only to the analytical chemist but to the separations chemist and chemical engineer as well.

Precipitation from Homogeneous Solution by LOUIS GORDON, MURRELL L. SALUTSKY and HOBART H. WILLARD, in ten tightly written chapters develops the historical background of the technique; describes the precipitation of hydroxides, basic salts, phosphates, oxalates, sulphates, sulfides and numerous miscellaneous compounds and evaluates the procedures; discusses coprecipitation and ways of minimizing the phenomena as well as ways of using it to advantage (for example in carrying radium on a barium precipitate); describes the use of this technique in fractional precipitation; and presents technological applications.

The presentation is a straightforward one with numerous illustrations from the literature; and the format makes for easy reading and reference. The authors are to be congratulated upon a book which is certain to prove of wide use to those with analytical or separations problems amenable to solution by the application of this technique.

DONALD F. PEPPARD

J. K. DAWSON and G. LONG: **Chemistry of Nuclear Power.** George Newnes, London, 1959. viii + 208 pp., 30s.

THIS book describes the important role played by the chemist in the development of nuclear power. As the authors point out in their preface, the engineers have received widespread recognition for their work, but it is not generally appreciated just how important has been the work of the chemist at all stages of the development of atomic energy into a large industry. Their work starts with the basic methods for the extraction and purification of raw materials, from which the reactor fuel elements are fabricated. Perhaps the most difficult task the chemist successfully solved was to produce a process for the separation of plutonium from irradiated uranium and fission products. Such a process was investigated by the use of only a few milligrams of plutonium and yet a full-scale plant handling tons of irradiated uranium was successfully planned and built on the results of such laboratory-scale experiments. Subsequently the chemists have been involved in problems of liquid and gaseous corrosion in chemical plant and reactor systems, the investigation of the compatibility of structural materials, and the methods of radioactive effluent disposal. These topics are briefly described and three chapters deal specifically with the chemical problems arising in nuclear reactors.

The last chapter discusses some future applications for the use of reactors and fission products. This is a subject which is now receiving widespread attention but is at an early stage of development. The possibility of using the kinetic energy of the fission fragments (84 per cent of the total energy of fission) to perform industrially important chemical reactions within the reactor is a fascinating project. The authors describe several possible reactions.

Vol.
15
1960

There is quite correctly no reference to the uses to which radioisotopes have been put in industry This subject is no longer new and has been adequately described elsewhere.

This book which is reasonably priced and well illustrated is strongly recommended to all chemists and also to nuclear engineers who require an understanding of the chemical problems of nuclear power.

G. R. HALL

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J. Inorg. Nucl. Chem., 1960, Vol. 15, p. 204. Pergamon Press Ltd. Printed in Northern Ireland

ERRATA

JOHN A. PANONTIN, ALBERT K. FISCHER and EDWARD A. HEINTZ: The preparation of mononitratodioxovanadium(V), VO_2NO_3, *J. Inorg. Nucl. Chem.* **14**, 145–147 (1960).

(a) Equation (1) on p. 146 should read:

$$V + 2N_2O_4 \xrightarrow[0°C]{CH_3CN} VO_2NO_3 \downarrow + 3NO \uparrow$$

(b) In the last paragraph on p. 147 the molar susceptibility should read:

$$+11{\cdot}6 \times 10^{-6} \text{ c.g.s.u.}$$

(c) For JOHN A. PANTONIN read JOHN A. PANONTIN.

Vol.
15
1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 205 to 209. Pergamon Press Ltd.

NEW RADIOACTIVE ISOTOPES OF THE RARE EARTH ELEMENTS

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(*Received* 26 *November* 1959)

Abstract—Three new radioisotopes have been made by spallation reactions in rare earth targets: ^{167}Lu, half-life 54 min, ^{161}Tm, 32 min, and ^{163}Tm, 2·0 hr, all decaying by electron capture.

A previously known ytterbium isotope of uncertain mass number has been assigned to ^{164}Yb, with a half-life of 85 min. A new radioactive terbium isotope decaying by *K* electron capture with a half-life greater than three years has been tentatively assigned to ^{158}Tb.

THIS paper describes a search for new neutron deficient radioisotopes of the rare earth elements produced by spallation reactions. The targets were usually 1 mg quantities of suitable rare earth oxides bombarded for 20 min in a 1 μA beam of 230 MeV protons. The rare earth spallation products were separated from one another by an ion exchange method similar to those of CHOPPIN and SILVA[1] and SMITH and HOFFMAN[2], i.e. elution with 0·4 M α-hydroxyisobutyric acid of pH 3·3–3·85 down a 12 per cent cross-linked Zeo-Karb 225 ion exchange column at 87°.

The product of a [*p*,*xn*] reaction could be isolated within 100 min of the end of an irradiation. The elution down the column required about 40 min.

LUTETIUM ISOTOPES

The resolution of the decay curves measured on a Geiger counter, for the lutetium fractions produced by bombardments of ytterbium oxide, yielded four components. Table 1 shows the correspondence between our half-life values and those previously reported in the literature.[3]

A new 54 min activity was found, but the 4·0 hr activity previously assigned to ^{172}Lu by WILKINSON and HICKS[4] was not observed. The mass assignment of the 54 min activity was made on the basis of a study of its decay products. The lutetium fraction isolated from irradiated Yb_2O_3 was allowed to decay for one hour and then a second ion-exchange separation was carried out to isolate the ytterbium daughter products. The decay of the ytterbium daughter fraction was followed on a Geiger counter and the gross decay curve was resolved into two components whose half-lives were 18 min and approximately 8 days. In another experiment the lutetium fraction separated from the Yb_2O_3 target was allowed to decay for 15 hr and a second ion-exchange separation was then performed. A thulium activity which decayed with a half-life of 9·2 days was obtained, but the ytterbium fraction contained no 18 min activity.

Absorption measurements in aluminium of the radiation from the lutetium indicated that there were no high energy positrons associated with the 54 min lutetium, a

[1] G. R. CHOPPIN and R. J. SILVA *J. Inorg. Nucl. Chem.* **3**, 153 (1956).
[2] H. L. SMITH and D. C. HOFFMAN, *J. Inorg. Nucl. Chem.* **3**, 243 (1956).
[3] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[4] G. WILKINSON and H. G. HICKS, *Phys. Rev.* **81**, 540 (1951).

conclusion confirmed by the absence of any annihilation radiation in the spectrum studied on a γ-scintillation spectrometer. No direct observation of K X-rays was made owing to the large contribution due to longer lived isotopes. HANDLEY and OLSON[5] have shown that ^{167}Yb has a half-life of 18·5 min and decays to 9·6 day ^{167}Tm, and our results are compatible with an assignment of the 54 min activity to ^{167}Lu decaying by electron capture.

$$^{167}\text{Lu} \xrightarrow[54\text{ min}]{\text{E.C.}} {}^{167}\text{Yb} \xrightarrow[18\text{ min}]{\text{E.C.}} {}^{167}\text{Tm} \xrightarrow[9.6\text{ days}]{\text{E.C.}} {}^{167}\text{Er [Stable]}$$

TABLE 1

This work. Half-lives	Literature values		
	Half-life	Mass number	Mode of decay
54 min			
1·3 days	approx. 2 days	^{169}Lu	E.C.
10 days approx.	8·1 days	^{171}Lu	E.C.
	and		
	6·7 days	^{172}Lu	E.C.
·20 days	1·4 years	^{173}Lu	E.C.
	and		
	165 days	^{174}Lu	E.C. and β^-

The γ-spectrum of the lutetium spallation products, examined on a scintillation spectrometer, showed three γ-rays of energies 120, 175 and 240 keV decaying out with a half-life of 54 min. HANDLEY and OLSON[5] found that ^{167}Yb decayed with emission of three γ-rays of energies 118, 180 and 330 keV, of which the first two are probably the same as the first two observed by us, since our ^{167}Lu would have been nearly in equilibrium with ^{167}Yb. The 240 keV γ-ray is probably associated with the decay of ^{167}Lu. ARON and his co-workers[6] have recently independently found this 54 min ^{167}Lu.

YTTERBIUM

The ytterbium spallation products of the bombardment of Tm_2O_3 were separated from the target and the resolution of the decay curves on a Geiger counter yielded five components (Table 2). The gross decay curves showed the growth of an 8 hr daughter from a 57 hr parent, and these half-life values agree well with those previously established for the ^{166}Yb-^{166}Tm pair.

The aluminium absorption measurements of the radiation from the ytterbium fraction indicated the presence of a 2·1 MeV positron (presumed) activity which decayed with a half-life of approximately 74 min. The γ-spectrum determined on a scintillation spectrometer showed a 0·51 MeV annihilation peak decaying with a single half-life of 85 min and a 94 keV γ-ray decaying with a half-life of approximately 80 min.

[5] T. H. HANDLEY and E. L. OLSON, *Phys. Rev.* **94**, 968 (1954).
[6] P. M. ARON, A. V. KALYAMIN, A. N. MURIN and V. A. YAKOVLEV, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **22**, 817 (1958).

Vol. 15 1960

An attempt was made to detect the thulium daughter of the 85 min ytterbium activity. The Tm_2O_3 target was allowed to decay for $3\frac{1}{2}$ hr after the end of the bombardment before the ytterbium fraction was isolated from it, so that the 18 min ^{167}Yb had decayed away and thus there was no possibility of confusing its daughter product with those of other short lived ytterbium nuclides. The isolated ytterbium fraction was then allowed to decay for 8 hr and the thulium daughter fraction separated. A single thulium activity with a half-life of 7·7 hours was obtained, which was almost certainly ^{166}Tm produced by the decay of 57 hr ^{166}Yb.

TABLE 2

This work. Half-lives	Literature values		
	Half-life	Mass number	Mode of decay
18 min	18·5 min	^{167}Yb	E.C.
85 min	74 min	$\gtrsim{}^{165}$Yb?	β^+
8 hr [daughter]	7·7 hr	^{166}Tm	E.C., β^+
57 hr [parent]	54 hr or 62 hr	^{166}Yb	E.C.
30 days	30·6 days	^{169}Yb	E.C.

In another experiment the ytterbium fraction isolated from irradiated Tm_2O_3 100 min after the end of the bombardment was allowed to decay for 1 hr and then the thulium daughter products were isolated by a second ion-exchange separation. The 7·7 hr ^{166}Tm and 9·6 day ^{167}Tm were observed but no short-lived thulium activities. These experiments suggested that the half-life of the daughter of the 85 min ytterbium is less than 15 min.

It will be shown in the next section that ^{161}Tm and ^{163}Tm have half-lives of 32 min and 2·0 hr, and are thus excluded as possible daughters of the 85 min ytterbium. HANDLEY and OLSON[5] have shown that the mass number of the previously known 74 min Yb positron emitter is less than 167. The most probable mass assignment of the 85 min activity is to ^{164}Yb. SUNYAR[7] listed a 90·5 keV transition in ^{164}Er and this could be the same as the 94 keV γ-ray observed by us, if an 85 min ^{164}Yb is decaying in equilibrium with a short ^{164}Tm which decays to ^{164}Er.

THULIUM ISOTOPES

The decay of the thulium fractions produced by proton bombardment of Er_2O_3 were followed on a Geiger counter (Table 3).

All but two, the 32 min and the approx. 1·9 hr activities, correspond closely with thulium nuclides previously reported in the literature.[3] A re-assessment of the half-life of the 1·9 hr activity is made later in the light of a knowledge of its mass assignment.

The aluminium absorption curves of the radiation from the thulium fraction indicated the absence of high energy positrons and β-particles. The γ-spectrum of the thulium fraction was complex and the detection of short-lived γ-rays was not possible

[7] A. W. SUNYAR, *Phys. Rev.* **98**, 653 (1955).

with the single channel analyser available, but the absence of the annihilation peak confirmed the absence of positrons.

The mass numbers of the 32 min and 1·9 hr thulium activities were determined from a study of their daughter products. The erbium daughter products which had grown into the thulium fraction after 1·5 hr decay were isolated and two erbium daughter products were detected, a 3 hr and a 70 min activity whose half-lives correspond closely with the previously reported 3·1 hr ^{161}Er and 75 min ^{163}Er. The 10 hr ^{165}Er daughter of 29 hr ^{165}Tm was not observed probably owing to the low counting efficiency of the radiation on a Geiger counter. In order to identify the erbium daughter activity produced by the decay of the approximately 1·9 hr thulium nuclide, an

TABLE 3

This work. Half-lives	Literature values		
	Half-life	Mass number	Mode of decay
32 min			
1·9 hr [approx.]			
8 hr	7·7 hr	^{166}Tm	E.C., β^+
29 hr	29 hr	^{165}Tm	E.C.
9·6 days	9·6 days	^{167}Tm	E.C.
>20 days	87 days	^{168}Tm	E.C.

irradiated Er_2O_3 target was allowed to decay for 5 hr before the initial separation of the thulium fraction, so that the 32 min thulium had decayed away. The thulium fraction was then isolated and allowed to decay for 2 hr before the erbium daughters were separated. The decay of this erbium fraction was followed on a γ-scintillation counter and found to consist of two components of half-lives 10 hr and 75 min. The 10 hr component was considered to be ^{165}Er produced by the decay of 29 hr ^{165}Tm and the 75 min component to be ^{163}Er from the decay of the 1·9 hr thulium, which must therefore be ^{163}Tm. Since the 3 hr ^{161}Er daughter was found only when the 32 min activity was present in the thulium fraction, the 32 min activity was assigned to ^{161}Tm.

The half-life of the new ^{163}Tm isotope as given above was determined as approximately 1·9 hr from the resolution of the gross decay curves, that is, in the presence of its 75 min ^{163}Er daughter. A calculation showed that a 2·0 hr parent decaying to a 75 min daughter would account for the experimentally observed curves, and accordingly the best value for the half-life of ^{163}Tm is considered to be 2·0 hr.

After this work was completed similar conclusions on the half-lives of ^{161}Tm and ^{163}Tm were independently reached by HARMATZ *et al.*[8]

A NEW LONG-LIVED TERBIUM ISOTOPE

Two attempts were made to produce and detect the isotopes ^{158}Tb and ^{157}Tb. Twenty-five milligrams of terbium oxide was bombarded with 380 MeV protons for 3 hr and the terbium fraction isolated 100 days later. The isolated terbium was carefully purified by three further ion-exchange separations to ensure the removal of all traces of the neighbouring elements gadolinium and dysprosium. The decay of the terbium fraction

[8] B. HARMATZ, T. H. HANDLEY and J. W. MIHELICH, *Phys. Rev.* **114**, 1082 (1959).

Vol. 15 1960

was followed for 2½ years on a Geiger counter, and the decay curve was resolved into an approximately 70 day activity and a long-lived activity which had a half-life greater than three years. The β-radiation from the 70 day activity was shown to have the same absorption characteristics in aluminium as a known sample of 72 day ^{160}Tb. The decay of the long terbium activity has not followed over a sufficient period of time to allow an accurate estimate of its half-life to be made. The possibility that this long activity was due to small amounts of long-lived contaminants of neighbouring elements was eliminated by mixing the terbium fraction with inactive carrier quantities of dysprosium and gadolinium. An ion-exchange separation was carried out on the mixture and the long-lived activity remained associated with the terbium fraction.

The γ-spectrum of the radiation emitted was measured with a scintillation spectrometer and showed only one peak at 41–42 keV, which is close to the value for the K X-rays of gadolinium.

The spallation reaction in terbium would produce a mixture of neutron deficient isotopes of terbium and also some 72 day ^{160}Tb produced by an $[n,\gamma]$ reaction, due to the considerable neutron flux produced in the accelerator. All the terbium isotopes of mass numbers 151–156 are known to have half-lives not greater than 5·6 days, so that, if possible isomerism is excluded, it seems probable that the new long lived terbium is either ^{157}Tb or ^{158}Tb decaying by K electron capture. An attempt was made to make ^{157}Tb by the process:

$$^{156}\mathrm{Dy}[n,\gamma]^{157}\mathrm{Dy} \xrightarrow[8\cdot2\ \mathrm{hr}]{\mathrm{E.C.}} {}^{157}\mathrm{Tb}.$$

66 mg of dysprosium oxide was irradiated for 28 days in a nuclear reactor in a flux of 10^{12} neutrons cm^{-2} sec^{-1}. No long lived terbium activity could be isolated from the irradiated material 120 days later. If our long lived terbium activity were ^{157}Tb, then for a neutron capture cross-section in ^{156}Dy of 100 millibarns or more the calculated yield of ^{157}Tb would have been at least as large as than from the spallation reaction, so that the failure to detect any terbium suggests that the long lived terbium is not ^{157}Tb, and consequently an assignment to ^{158}Tb seems plausible. However, no very certain argument can be made on the basis of the relative yields for the spallation and neutron irradiation, since multiple traversals of the target by the proton beam may occur to an unknown extent, and also the cross section for neutron capture by ^{156}Dy is not known.

Our results are not inconsistent with the conclusions of HANDLEY and LYON[9] who concluded that the half-life of ^{158}Tb was either less than 10 min or greater than 5 years, and of HANDLEY and OLSON[10] who concluded that the half-life of ^{157}Tb was either less than 30 min or greater than 100 years.

[9] T. H. HANDLEY and W. S. LYON, *Phys. Rev.* **99**, 1415 (1955).
[10] T. H. HANDLEY and E. L. OLSON, *Phys. Rev.* **90**, 500 (1953).

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 210 to 214. Pergamon Press Ltd.

THE URANIUM Z/URANIUM X_2 BRANCHING RATIO

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(*Received* 8 *January* 1960)

Abstract—The UZ/UX_2 branching ratio in the natural uranium decay series has been measured using a 4π counting method in conjunction with ^{231}Pa as tracer and found to be (0·18 ± 0·02) per cent.

URANIUM Z, the ground state of ^{234}Pa, was discovered in 1921 by HAHN[1], who, with several other early workers, made measurements of the proportion of the decays in the natural uranium series which proceed through this nuclide, rather than directly from the isomeric (upper) state, UX_2. The early measurements[2,3] gave results of 0·33 per cent and 0·35 per cent for this proportion but both results involved not-too-precisely-known instrumental calibrations.

FEATHER and BRETSCHER[4], using the co-precipitation of protactinium with tantalic acid to separate $UZ + UX_2$ from UX_1, followed by the measurement of the two fractions with an end-window Geiger-Müller tube, obtained a value of (0·15 ± 0·015) per cent and this was apparently confirmed in essentials by the later work of BRADT and SCHERRER[5], who, following the increase of the γ-activity of a UX_1 solution from which the UZ had been removed, obtained a value of 0·12 per cent. More recently doubt has been thrown on these values by the measurements of SIZOO *et al.*[6] (using a cation exchange method devised by BARENDREGT and TOM[7]) which gave a value of (0·63 ± 0·063 per cent). In view of the discrepancy so revealed, a re-determination has been carried out, using two different chemical procedures, and making the final counting measurements with a 4π proportional counter. Chemical yields have been estimated through the addition of trace amounts of the long-lived α-emitting ^{231}Pa.

Two methods were used to separate protactinium and thus UZ from UX_1. The first was a solvent extraction procedure described by GOLDEN and MADDOCK[8], in which protactinium is extracted from 6 to 8 N hydrochloric acid by di-isopropyl ketone (DIPK) and can be back extracted into an aqueous hydrochloric acid phase containing fluoride. Thorium is not extracted into the organic layer under these conditions. The second separation depends on the observation by KRAUS *et al.*[9] that protactinium is readily adsorbed on a strong base anion exchange resin from 9 N hydrochloric acid. Thorium is not adsorbed and is washed out of the resin bed with large volumes of hydrochloric acid without affecting the protactinium. Uranium, if

[1] O. HAHN, *Ber. Dtsch. Chem. Ges.* **54**, 1131 (1921).
[2] O. HAHN, *Z. Physik. Chem.* **103**, 461 (1923).
[3] W. G. GUY and A. S. RUSSELL, *J. Chem. Soc.* 2618 (1923).
[4] N. FEATHER and E. BRETSCHER, *Proc. Roy. Soc.* A **165**, 530 (1938).
[5] H. BRADT and P. SCHERRER, *Helv. Phys. Acta* **18**, 405 (1945).
[6] F. BARENDREGT and SJ. TOM, *Physica* **17**, 817 (1951).
[7] W. L. ZIJP, SJ. TOM and G. J. SIZOO, *Physica* **20**, 727 (1954).
[8] J. GOLDEN and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **2**, 46 (1956).
[9] K. A. KRAUS, G. E. MOORE and F. NELSON, *J. Amer. Chem. Soc.* **78**, 2692 (1956).

Vol. 15 1960

present, will be held with the protactinium, but the latter is easily eluted from the column under conditions where the former remains adsorbed.

As some of the protactinium sources obtained in the earlier experiments contained appreciable residues, absorption measurements were made to enable a correction to be applied for self-absorption of α- and β-radiation.

EXPERIMENTAL

Outline of the branching ratio determination

About 2–2·5 ml of a UX solution containing approximately 0·5 μc were split into two weighed portions. The small portion, about one fifteenth of the total, was reserved for measurement of the UX_2 content by liquid counting. A measured volume of ^{231}Pa solution (containing about 1000 disintegrations/min) was added to the larger portion and protactinium separated as described below and deposited on a prepared 4π source film. The activity of this source was followed by absolute counting over about 25 hr in a 4π proportional counter, and the UZ activity resolved graphically from the background of ^{231}Pa and uranium X (which was small in amount). The same measured volume of ^{231}Pa solution was deposited directly on another 4π source film and the chemical yield of the UZ separation was determined by counting this source and comparing with the decayed UZ + ^{231}Pa source using an α-scintillation counter. From the UZ decay curve extrapolated back to the time of the separation from the UX solution, the initial UZ activity of the source was obtained, and from the chemical yield the UZ activity of the original UX solution was calculated. The ratio of the UZ activity to the UX_2 activity of this solution calculated from the UX_2 activity of the smaller portion of UX solution gave the branching ratio.

Counting equipment

Liquid counting was performed using a halogen quenched Geiger-Müller liquid counter type M.6H.

4π counting was carried out using a pair of cylindrical proportional counters, 3·5 cm dia. × 2·5 cm deep, between which the source was sandwiched.[10] Methane (10 per cent)–argon (90 per cent) mixture was passed continuously through the counters, which were connected to a linear amplifier type 1008. The α-scintillation counter, type 1093A, used a ZnS scintillator and EMI multiplier phototube type VX 5045 and had an efficiency of about 30 per cent for counting ^{231}Pa α-particles. In each case, disintegrations were recorded (after any necessary discrimination against noise) on a scale-of-100.

Preparation of 4π sources

Sources for 4π counting and for α-scintillation counting were deposited on VYNS films prepared by the method of PATE and YAFFE[11] and stretched across flat aluminium rings 1·5 in. outside diameter and 1 in. inside diameter. The superficial density of the VYNS films was 5–10 μg/cm^2. One side was coated with not more than 5 μg/cm^2 of gold and about 1 cm^2 of the centre of the opposite side was treated with insulin.

Calibration of the liquid counter

About 50–80 mg of "aged" uranium oxide were weighed and dissolved in 2 N nitric acid with the addition of 3–4 drops of 9 N hydrochloric acid. The solution was diluted to 12 ml in a graduated flask and 10 ml pipetted into the liquid counter. The counter efficiency was calculated assuming that only UX_2 β-particles were counted and that the UX_2 was in secular equilibrium with UX_1 and ^{238}U.

Preparation of the uranium X solution

The bulk of the uranium from 20 g AR uranyl nitrate was removed by stirring with water saturated ether. Traces of ether were expelled from the residual aqueous solution by warming and

[10] R. C. HAWKINGS, W. F. MERRITT and J. H. CRAVEN, *Proc. of Symposium on Maintenance of Standards, N.P.L., May* 1951. H.M.S.O., London (1952).
[11] B. D. PATE and L. YAFFE, *Canad. J. Chem.* **33**, 15 (1955).

then 10 ml of 9 N hydrochloric acid were added. The solution was placed on a column 30 cm long, 1 cm diameter, of Dowex-1 X10, anion exchange resin, 100–200 mesh, and the column eluted with 9 N hydrochloric acid. The UX in the eluant (about 1 l.) was concentrated by evaporation until the residue was 1–2 ml. Organic material, if present, was destroyed with nitric acid and the UX was finally taken up in a few millilitres of 9 N hydrochloric acid after removing any remaining nitric acid. A 150 mg portion of the solution on dilution to 10 ml with 2 N nitric acid gave a counting rate of 4000–8000 c.p.m. in a liquid counter having a counting efficiency of about 10 per cent.

Separation of uranium Z from the uranium X solution

(a) *By solvent extraction.* The larger portion of the UX solution was transferred to a small polyethylene test tube and the ^{231}Pa solution was added. The ^{231}Pa solution contained fluoride and about 10 mg of aluminium chloride was added to destroy fluoro complexes of protactinium. The solution was vigorously agitated for 6 min with 2–3 ml of DIPK. The stopwatch indicating the time from the instant of separation of UZ from the remaining UX solution was started when the two phases separated after agitation. The aqueous layer was discarded and the organic layer, occasionally replenished by the addition of further small amounts of DIPK was washed five times with 2 ml portions of 9 N hydrochloric acid. Protactinium was stripped from the organic layer by agitating with 3 ml of a solution N in hydrochloric acid and 0·5 N in hydrofluoric acid, and the aqueous extract washed with two portions each about 2 ml of ether before evaporation in a platinum crucible. When the residual solution was reduced to 1–2 drops as much as possible was transferred to a 4π source film and evaporated to dryness. The separation and preparation of the source required 90–120 min but the effective time of separation of the UZ from its parent substance was certainly known to within 3 min.

(b) *Ion exchange.* A column of Dowex-1 X10 anion exchange resin, 100–200 mesh, 6 cm long, was prepared in 9 N hydrochloric acid. The column was supported on a sintered polyethylene disc placed about 0·5 cm from the end of a polyethylene tube, 21 cm long and 0·7 cm internal diameter. The UX from which the UZ was to be separated together with the tracer ^{231}Pa was treated with aluminium chloride or evaporated repeatedly with 9 N hydrochloric acid to remove fluoride. It was then placed on the column and permitted to permeate slowly into the resin bed for about 2 min. A 9 N hydrochloric acid reservoir was attached at the top of the column and a positive pressure increasing gradually to 25–30 cm of mercury was applied during the collection of the first effluent sample. The 10 ml samples were collected while maintaining this pressure throughout the separation. The flow rate was 3–5 ml per min. A stopwatch was started as soon as effluent emerged from the column and the time noted at which each of the numbered samples was collected. The β-activity in these samples, measured using a liquid counter allowed the time of the initial crude separation to be estimated to within 5 min and also indicated when the column had been freed from β-activities other than UZ. Some 300–400 ml of hydrochloric acid were required for each separation. The protactinium was stripped from the column with 6 ml of a mixture 9 N in hydrochloric acid and 1 N in hydrofluoric acid. As before this effluent was concentrated to 1–2 drops and then evaporated to dryness on a 4π source film. The time required for this separation and preparation of the source was from 120 to 150 min.

Purification and preparation of the ^{231}Pa solution

Before use the ^{231}Pa was purified from α-emitting daughters by the method described by Golden and Maddock[8]. The solution strength was adjusted so that 0·1 ml contained a ^{231}Pa activity of about 1000 disintegrations/min.

UX_2 *activity*

The smaller weighed portion of UX solution was diluted to 12 ml with 2 N nitric acid and 10 ml measured into the calibrated liquid counter. From the β-activity of this solution and the counter efficiency, the UX_2 activity of the larger portion of UX solution was calculated.

Source absorption measurements

None of the sources used for counting was thicker than 300 μg/cm^2 and those from ion-exchange separated material were considerably thinner. Self-absorption of α- and β-particles in the source

material was thus unlikely to be a major source of error and, in any event, the corrections for absorption of the two types of particle operate in opposite directions and tend to cancel one another.

Corrections have nevertheless been estimated and applied to the observed results. In the α-particle case, sources were made containing aliquot portions of the carrier-free ^{231}Pa solution with varying quantities of K_2NbF_7. These were counted on the α-scintillation counter, and a curve of counting efficiency against source superficial density prepared. Only relative measurements are needed in this instance, as the ^{231}Pa activity is used as a "tracer" only, and absolute efficiency factors do not enter the final calculation.

For the UZ β-particles it was not found possible to prepare enough material at a sufficiently high specific activity, and the experimental points measured by a method analogous to that used for the α-particle case could not be rendered absolute. A curve was therefore constructed using self-absorption data obtained for ^{35}S (which has a β-energy very similar to that of the lowest energy group from UZ), and the published data of MERRITT *et al.* [12] obtained for a variety of β-emitters using a counter very similar to ours. The four β-branches of the UZ decay were weighted according to the relative abundances determined by HOK *et al.*[13] It may be noted that the lowest-energy β-particle group in UZ (which will be subject to the greatest uncertainty in correcting for self-absorption) occurs in only 28 per cent of the disintegrations.

RESULTS AND DISCUSSION

Twelve independent measurements were made, with results indicated in the table. Four used the solvent extraction method, and the remainder the ion-exchange procedure for isolating the UZ. The latter gave thinner final sources for counting, and the results obtained from them are thought to be the more reliable.

Exp. no.	Chem.* sep'n.	Chem. yield (%)	Branching ratio (uncorr.) (%)	Source† thickness (μg/cm²)	Self-absorption correction factor	Branching ratio (corr.) (%)
1	S.E.	22·2	0·24	300	0·81	0·19
2	S.E.	15·2	0·23	300	0·81	0·19
3	S.E.	25·6	0·23	300	0·81	0·19
4	S.E.	35·2	0·21	200	0·85	0·18
5	I.E.	30·8	0·22	200	0·85	0·19
6	I.E.	40·4	0·21	200	0·85	0·18
7	I.E.	44·3	0·18	50	0·94	0·17
8	I.E.	30·9	0·16	50	0·94	0·15
9	I.E.	16·9	0·18	50	0·94	0·17
10	I.E.	33·1	0·18	50	0·94	0·17
11	I.E.	‡6·51	0·17	50	0·94	0·16
12	I.E.	41·1	0·18	50	0·94	0·17

* S.E. = solvent extraction. I.E. = ion exchange.
† Estimated visually by comparison with weighed sources.
‡ Part of this source was lost in the course of preparation.

Separations of UZ from UX_1 (made by ion exchange) without the addition of ^{231}Pa tracer showed small but measurable α-activities. Although not completely reproducible this contamination represented 3–5 per cent of the ^{231}Pa activity, and a correction of 4 per cent has been applied to allow for its presence in these cases. The solvent extraction experiments showed a negligible effect of this nature.

[12] J. S. MERRITT, J. G. V. TAYLOR and P. J. CAMPION, *Canad. J. Chem.* **37**, 1109 (1959).
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The average value obtained for this branching ratio is (0·18 ± 0·02) per cent. The error quoted is larger than is called for by the observed spread of results, and includes a small margin for possible systematic errors. These are considered likely to be small since

(a) the absolute measurement of the UZ β-particles has been made by the 4π counting technique under rather favourable conditions.

(b) the use of the long-lived α-emitting ^{231}Pa removes the possibility of confusion between incompletely removed UX_1 (half-life 24·1 days) and the tracer protactinium (e.g. ^{233}Pa, half-life 27·4 days).

(c) chemical yields have been reasonably high throughout the measurements.

The results appear essentially to confirm the early measurement of FEATHER and BRETSCHER[4] and cast doubt on the more recent value of SIZOO *et al.*[7]

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Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 215 to 221. Pergamon Press Ltd.

A RAPID METHOD FOR THE DETECTION OF ^{90}Sr CONTAMINATION IN ^{90}Y*

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Abstract—Yttrium-90, milked from its parent ^{90}Sr, may be tested rapidly and simply for the presence of ^{90}Sr contamination. After adding Y and Sr carriers, an aliquot is passed through a column of Dowex 1 × 10 in the hydroxyl form, and a portion of the effluent is evaporated to dryness and counted with and without absorber. Requiring less than 1 hr to perform, the method detects as little as 0·02 μc ^{90}Sr in 100 mc ^{90}Y. Larger aliquots can be used for even greater sensitivity. The mechanism of bonding the Y to the resin is shown to be via an yttrium-citrate complex. The performance of resins of other cross-linkages and in forms other than hydroxyl is discussed.

YTTRIUM-90 is a radioisotope of interest to workers in the medical field. Considerable research has been done with it, and it shows promise for certain applications in cancer therapy.[1] It should also be of value as a tracer in industrial research, since it is a pure beta emitter with a relatively short half-life.

In the interest of making ^{90}Y more readily available, and available at a much lower price per millicurie than it is at present, a method[2] has been developed at Brookhaven by means of which ^{90}Y can be milked from its long-lived parent, ^{90}Sr. The method is simple, rapid and safe, and gives a ^{90}Y product that is contaminated with less than 10^{-6} per cent of ^{90}Sr. Despite the low level of this contamination, the hazardous nature of ^{90}Sr makes it imperative that the user know positively that its level is well below the point where there would be any hazard to either patients or attending personnel. The standard radiochemical method[3] for the determination of the low level of strontium present, which involves removing the yttrium by multiple precipitations of yttrium hydroxide, would require the use of the entire product solution as sample, and would take a competent radiochemist several hours to perform. Alternatively, ^{90}Sr could be determined after waiting several weeks for the $^{90}Y$to decay. Neither method permits the determination of ^{90}Sr in a ^{90}Y solution before it is administered to a patient.

The present assay can be run in an hour or less, requires only a small portion of the product for a sample, needs no special skill, radiochemical or otherwise, on the part of the clinical technician who will be doing the analysis, and under the conditions chosen will detect as little as 0·02 μc ^{90}Sr in the presence of 100 mc ^{90}Y.

* This work was performed under the auspices of the U.S. Atomic Energy Commission. Part of the material contained herein was presented at the Symposium on Radiochemical Analysis, Division of Analytical Chemistry, American Chemical Society, 136th National Meeting, Atlantic City, N.J., September, 1959.

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THE BROOKHAVEN METHOD FOR MILKING YTTRIUM-90 FROM STRONTIUM-90

The parent–daughter pair, ^{90}Sr and ^{90}Y, provides the basis for an almost ideal milking system. The parent has a long half-life (28 years) so that its decay may be neglected. The daughter has a half-life (64 hr) that is long enough to permit work to be done conveniently in many biological and physiological systems; at the same time it is short enough to permit the isotope to be placed within the body, to provide a source of local radiation, and be left there to decay away. (After 20 days less than 1 per cent of the activity remains.) The short half-life also permits usable quantities of ^{90}Y to be formed in reasonable lengths of time. For example, 94 per cent of equilibrium is attained in 10 days, and 20 per cent is reached in 24 hr. That is, 20 mc of ^{90}Y can be milked daily from a 100 mc source of ^{90}Sr.

While ^{90}Y is available from Oak Ridge and commercial suppliers, or can be made by irradiating very pure yttrium oxide in a reactor, it is relatively expensive from these sources especially when used in the quantities necessary for therapy. The Brookhaven method whereby carrier-free ^{90}Y can be milked from ^{90}Sr by the user in his own laboratory as desired not only cuts the cost tremendously but also permits storing a short-lived isotope "on the shelf" until needed, with no loss by decay.

Two microcuries of ^{90}Sr fixed in the bone is the current lifetime tolerance.[4] Consequently to be acceptable a milking system must leave an extremely low ^{90}Sr contamination in the product ^{90}Y. The method developed accomplishes the separation by means of a Dowex-50 ion-exchange column. While others[5] have reported the separation of yttrium from strontium by ion-exchange and still others[6–12] have reported other separation methods, none have attained a satisfactorily high separation for this application. The Brookhaven method gives a product in which the ratio of ^{90}Sr to ^{90}Y is less than 10^{-6}. This corresponds to a contamination of 0·001 μc of ^{90}Sr in 100 μc of ^{90}Y. The ^{90}Sr concentration of 10^{-5} μc/cm^3 in the product solution is only a factor of ten higher than the 10^{-6} μc/cm^3 that is considered permissible for the continuous lifetime ingestion in drinking water.[4] A column of Dowex-50 X8, 50–100 mesh, 3·5 cm in diameter and 18 cm high, in the hydrogen form, is loaded with the desired amount of ^{90}Sr solution, and washed with 4 l. of eluting solution. This is a 0·5 per cent citric acid solution, the pH of which has been adjusted to 5·5. This pH adjustment is quite critical. After allowing the ^{90}Y to grow in, it is eluted with 100 ml of the same solution. Flow rate of the eluting solution is adjusted to 4 ml/min. Under these conditions, a ^{90}Y yield of greater than 98 per cent is obtained in less than one-half hour. Milkings have been made on the same column over a period of two years, with no serious increase in the contamination level. The normal loading has been 100 mc, but amounts up to 1·5 c have been placed on a single column.

DESCRIPTION OF ASSAY METHOD

Although the many milkings made on several columns over a period of two years provided no case where the ^{90}Sr ran higher than normal, nevertheless, on ^{90}Y solutions that are to be administered to patients, it is necessary to be able to establish that the contamination in any given milking is no higher than some agreed-upon safe maximum, for the protection both of the patients and of people operating the milking device.

The method developed involves using an anion exchange resin to remove the bulk of the ^{90}Y as a citrate complex from an aliquot of the product solution. The strontium is unaffected by the resin, passes through, and is counted.

A 5 ml aliquot of the yttrium product solution is taken. To this is added a solution containing 3·5 mg of yttrium carrier and 2 mg of strontium carrier. The solution is then run through a Dowex-1

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Vol. 15 1960

X10, 50–100 mesh, resin in the OH^- form in a column 1 cm in diameter by 10 cm high. A decontamination factor of about 10^7 is obtained with respect to the ^{90}Y, while the ^{90}Sr is unaffected. The effluent from the column is caught in a volumetric flask and sufficient wash water is passed through the column to bring the volume up to 25 ml. A 2 ml aliquot of this is taken and evaporated to dryness on a planchet which is then counted with an end-window β-counter, once with and once without a 220 mg/cm^2 aluminium absorber interposed. The absorber removes the ^{90}Sr betas, allowing only the betas from the small residual amount of ^{90}Y to be counted. A previously determined factor is applied to correct for the partial absorption of the yttrium betas by the absorber, and the difference between this corrected count and the count without absorber gives the counts from any ^{90}Sr present. Applying the usual corrections for geometry, etc. gives the activity.

This method should detect as little as 0·02 μc of ^{90}Sr in the presence of 100 mc of ^{90}Y. While this is a factor of about twenty higher than the normal contamination level, it is well below the point where there would be any serious hazard, even if the entire 100 ml of product solution were ingested. In practice the presence of a detectable amount of ^{90}Sr would indicate that something was wrong with the operation of the milking unit, and it would be thoroughly investigated before further use was made of it.

EXPERIMENTAL RESULTS

At the beginning of the work, a column size that appeared to be convenient for the application was arbitrarily selected. This was a column 1 cm in diameter by 10 cm high, loaded with 10 g of 50–100 mesh Dowex-1 resin. The resin, in the chloride form when received, was converted to the hydroxyl form by slowly passing through the column 100 ml of 2 N NaOH followed by 100 ml of water.

The feed material for the columns was ^{90}Y solution, containing 0·5 weight per cent citrate ion, that had been milked from a Dowex-50 column loaded with about 100 mc of ^{90}Sr. This solution was therefore typical of the product solutions that would be used ultimately. A 5 ml sample was taken for each assay, each sample containing between 3 and 5 mc of ^{90}Y. (In the cases where citrate-free yttrium solutions were used, the citrate ion was destroyed by taking the solution nearly to dryness after the addition of nitric and sulphuric acids.) To the 5 ml product sample were added solutions containing 2 mg of strontium carrier and the desired amount of yttrium carrier. The yttrium carrier added ranged from zero (carrier-free) to 10·6 mg. The resultant solution was poured onto the top of the resin column, and the flow rate adjusted until the effluent was leaving the column at the rate of 2 ml/min. The sample was followed with wash-water, at the same flow rate, until a total of 25 ml had been collected. Two millilitres of this solution were taken to dryness and counted.

In the early work, ^{90}Sr analyses were run, but more recently, the result of interest has been the ^{90}Y decontamination factor (D. F.), inasmuch as the ^{90}Sr analyses showed essentially no strontium hold-up on the columns. The D. F. is defined as the ratio of the ^{90}Y activity put into the column to the ^{90}Y activity leaving the column. The higher the D. F., the more ^{90}Y which has been removed by the column, and the smaller the amount of ^{90}Sr activity that can be detected.

The first resin used, and the one upon which the assay method was based, was some Dowex-1 that had been around the laboratory for several years. The resin was unlabelled with respect to cross-linkage but was assumed to be 8 per cent. With this resin, D. F.'s of about 10^5 were obtained with 2 mg of Y carrier. When this resin began to run out, a second batch was ordered and received about a year ago, 8 per cent cross-linkage being specified this time. With this new material, the D. F.'s at first were variable and less than 10^4. It was then suspected that the cross-linkage of the resin and possibly the amount of yttrium carrier added affected the D. F., and, therefore, a systematic study was made of the various cross linkages of Dowex-1 resin that were available. Runs were made carrier-free and with various amounts of added yttrium carrier. The amounts of strontium carrier and citrate ion present were held constant at 2 mg and 25 mg, respectively.

The results of these runs are shown in Table 1, and are plotted in Figs. 1–7.

Experiments were also run with ^{90}Y solution from which the citrate ion was removed before the solution was run through the Dowex-1 column. These results are shown in Table 2.

A third series of runs was made, with the 10 per cent cross-linked resin in forms other than

Table 1.—Decontamination factor of Dowex-1 as a function of cross-linkage and amount of carrier

Dowex-1 cross-linkage (%)	Yttrium/citrate mole ratio					
	0·0	0·042	0·087	0·17	0·46	0·92
2	$3·6 \times 10^{5}$	$8·2 \times 10^{5}$	$1·4 \times 10^{6}$	$2·5 \times 10^{6}$	$3·9 \times 10^{5}$	$8·2 \times 10^{3}$
4	$8·4 \times 10^{4}$	$3·6 \times 10^{5}$	$9·3 \times 10^{4}$	$8·4 \times 10^{3}$	$4·1 \times 10^{3}$	$9·6 \times 10^{3}$
8*	$1·1 \times 10^{5}$	$5·4 \times 10^{5}$	$3·1 \times 10^{5}$	$5·2 \times 10^{5}$	$1·1 \times 10^{3}$	2·8
8†	$5·7 \times 10^{4}$	$2·2 \times 10^{5}$	$5·7 \times 10^{3}$	$3·3 \times 10^{4}$	4·0	1·9
8‡	$3·4 \times 10^{5}$	$3·0 \times 10^{5}$	$3·7 \times 10^{5}$	$6·9 \times 10^{6}$	$2·6 \times 10^{3}$	0·95
10	$9·5 \times 10^{5}$	$2·6 \times 10^{5}$	$1·9 \times 10^{5}$	$5·7 \times 10^{5}$	$1·1 \times 10^{7}$	$1·1 \times 10^{6}$
16	$9·9 \times 10^{3}$	$3·9 \times 10^{1}$	2·2	1·4	1·0	0·95

* Cross-linkage unknown but presumed to be 8%.
† Received 1958.
‡ Received 1959.

Table 2.—Decontamination factor of Dowex-1 in citrate-free solution

Dowex-1 cross-linkage (%)	Weight of yttrium carrier added*, (mg).					
	0·0	0·5	1·0	2·0	5·3	10·6
2	14	1·1	1·2	3·7	1·5	1·4
8	3·3	1·1	1·1	1·3	1·6	1·6
16	2·2	1·1	1·2	1·3	2·0	2·8

* The corresponding columns of this table and of Table 1 contain the same amount of yttrium carrier; e.g. in Table 1 a Y/Cit. mole ratio of 0·042 is achieved by adding 0·5 mg of Y carrier.

Table 3.—Decontamination factors, Dowex-1 X10

Form	No Y carrier		2 mg Y carrier	
	Citrate	No citrate	Citrate	No citrate
carbonate	$1·4 \times 10^{5}$	$3·5 \times 10^{3}$	$9·5 \times 10^{5}$	$1·2 \times 10^{3}$
hydroxyl	$9·4 \times 10^{3}$		$5·7 \times 10^{6}$	
citrate	$2·1 \times 10^{4}$	$2·0 \times 10^{3}$	$2·0 \times 10^{4}$	$2·0 \times 10^{3}$
chloride	$3·4 \times 10^{3}$	1·1	$3·4 \times 10^{3}$	1·0
sulphate	$2·5 \times 10^{3}$	$2·8 \times 10^{1}$	$6·4 \times 10^{1}$	1·2
nitrate	$4·3 \times 10^{3}$	1·1	$3·4 \times 10^{1}$	1·0

the hydroxyl. The resin was conditioned in the carbonate, citrate, chloride, sulphate and nitrate forms. These results are shown in Table 3, with some of the hydroxyl data included for reference.

DISCUSSION

It should be borne in mind that in the work presented here, the endeavour was to obtain a practical analytical method that would work simply, rapidly and reproducibly. Consequently, studies were limited to the particular column adopted for use, rather than being made on more general systems from which more fundamental

Vol. 15 1960

data might have been obtained. However, some conclusions may nevertheless be drawn from the data obtained.

It is evident that the yttrium is bound to the resin as an yttrium citrate complex, because

(1) the resin is an anion exchange resin,
(2) the D.F.'s in citrate-free solutions are very much lower than in the comparable case where citrate ion is present (see Table 2), and
(3) with the resin in the citrate form, the D. F. is still quite high (Table 3).

These facts would rule out the precipitation of yttrium hydroxide locally as the mechanism (previously suggested[13]) by which yttrium is retained on a basic column.

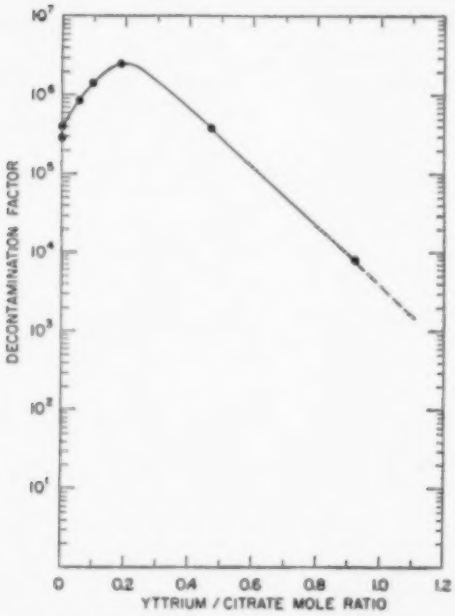

FIG. 1.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 50–100 mesh, OH^- form: 2 per cent cross-linkage.

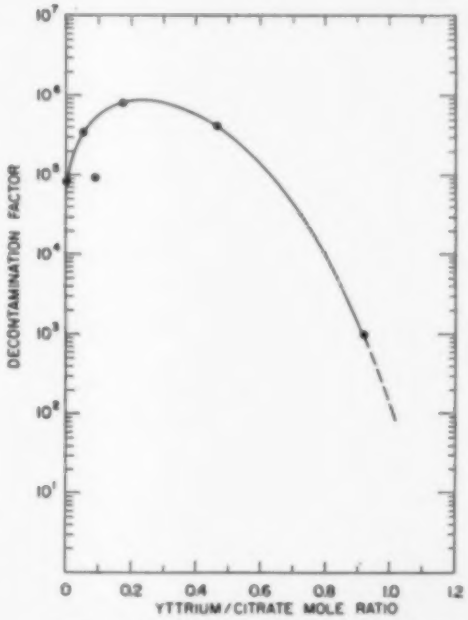

FIG. 2.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, <50–100* mesh, OH^- form: 4 per cent cross-linkage.

It will be noted that all of the curves in Figs. 1–7, showing the relation between D. F. and amount of yttrium carrier present for each of the cross-linkages available, exhibit a rise to a maximum somewhere between yttrium to citrate ratios of 0·2 and 0·4, with the exception of the 16 per cent resin. It is possible that even this curve also goes through a maximum, close to zero grams of carrier, but the data are not sufficiently complete to show it. The dropping off of the D. F.'s at higher yttrium to citrate ratios is undoubtedly because there is insufficient citrate ion present to form the appropriate yttrium complex. Either some of the yttrium is not complexed at all, or a complex is formed that is less tightly bound to the resin. In either case, at these

* Nominal 50–100 mesh when received; resin was backwashed with water prior to use in order to improve flow characteristics; this removed 50 per cent of resin by weight as fine particles; used same wet volume of this washed resin for each assay as was used for other resins.

[13] H. L. FINSTON and J. MISKEL, *Ann. Rev. Nucl. Sci.* **5**, 274 (1955).

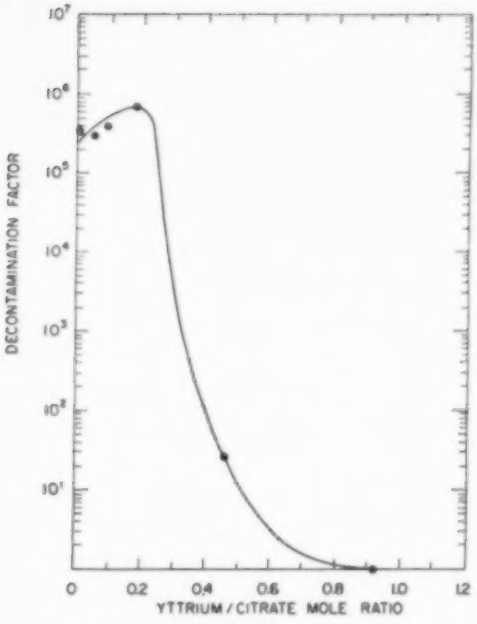

FIG. 3.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 20–50 mesh, OH^- form: 8?%* cross-linkage.

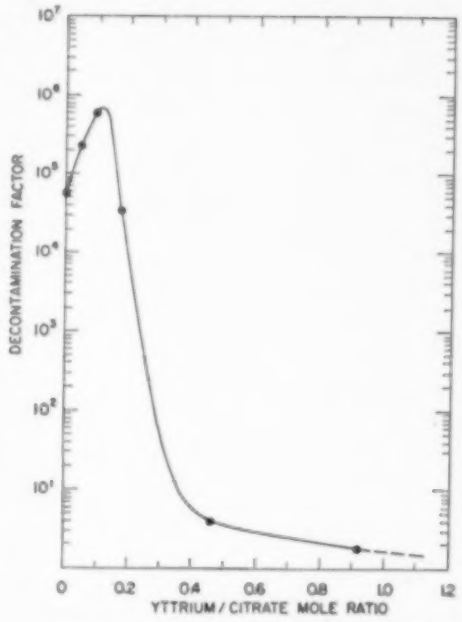

FIG. 4.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 50–100 mesh, OH^- form: 8% cross-linkage (new batch, received 1958).

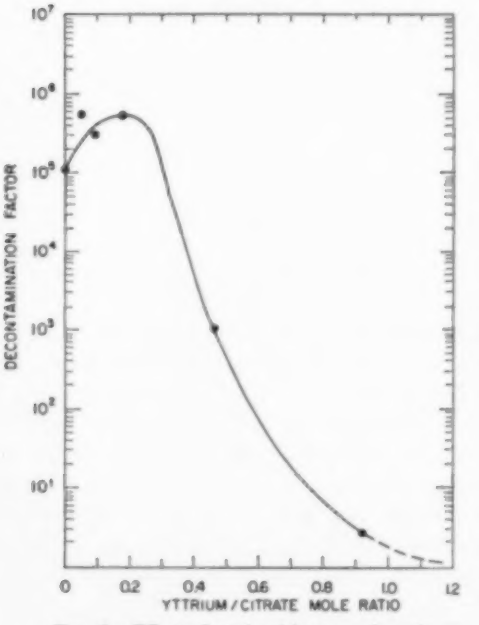

FIG. 5.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 50–100 mesh, OH^- form: 8% cross-linkage (latest batch, received 1959).

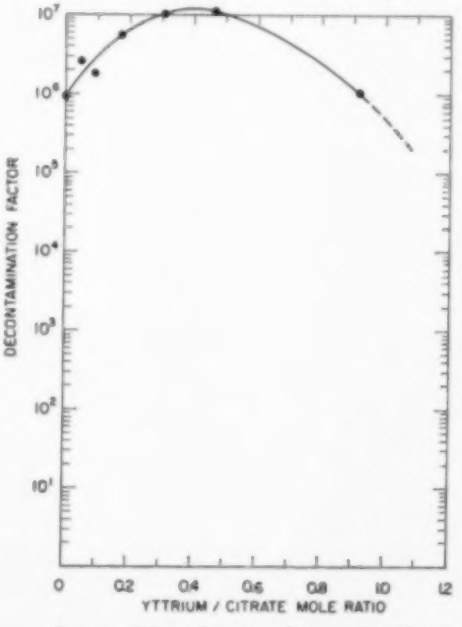

FIG. 6.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 50–100 mesh, OH^- form: 10% cross-linkage.

* Original resin re-run July, 1959. Cross-linkage unspecified and uncertain but presumed to be 8%.

Vol. 15 1960

high Y/citrate ratios some of the yttrium leaks through the column. This yttrium leakage is not a result of the capacity of the resin being exceeded, since the column capacities range from 6 to 13 milliequivalents for the various cross-linkages, while the maximum yttrium run through any column was 0·36 milliequivalents and the citrate ion was constant at 0·39 milliequivalents.

Why the curves rise from the carrier-free condition to a maximum is not readily explained. It may be possible that a complex having a high citrate/yttrium ratio is formed which, because of its size, is less tightly bound to the resin than another

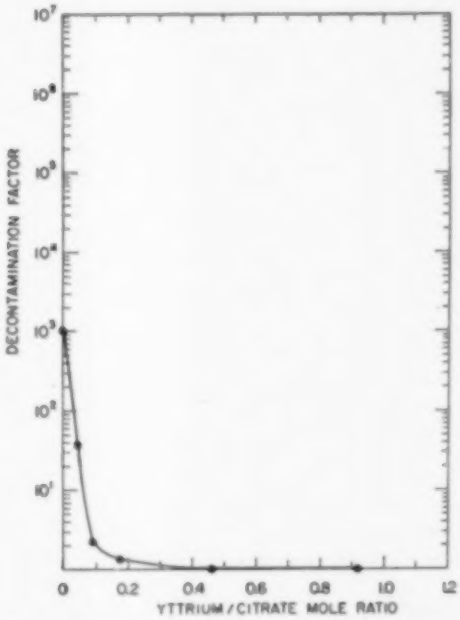

FIG. 7.—Effect of yttrium/citrate mole ratio on decontamination factor: Dowex-1 anion exchange resin, 50–100 mesh, OH^- form: 16% cross-linkage.

complex having a somewhat lower citrate/yttrium ratio. At any rate, the system is quite complicated, involving equilibria between the yttrium ion, the hydrogen ion, the various citrate ions and the complexes that may be formed between them and the resin, which itself may be in either hydroxyl or citrate forms, and so on. At the present time, there is insufficient information from which to infer anything regarding the composition of the complex most tightly bound to the resin.

It is of interest to compare the three 8 per cent curves: the original resin, the resin obtained about a year ago, and the most recent resin obtained. The three curves are similar in shape, but the second one is displaced slightly to the left. The amount of yttrium carrier originally used fell on the steep portions of these curves. This is why the two batches of resin at first did not appear to behave similarly.

On the basis of this work, the 10 per cent resin will be used for the routine analysis, with 3·5 mg of yttrium carrier being added (yttrium/citrate mole ratio = 0·30). A D. F. of 10^7 is obtained routinely, and there is a broad plateau so that small variations in carrier concentration are insignificant. This will permit the detection of 0·02 μc ^{90}Sr in the presence of 100 mc of ^{90}Y.

Acknowledgement—The assistance of J. DAANE in obtaining some of the data is acknowledged.

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 222 to 236. Pergamon Press Ltd.

RADIOCHEMICAL STUDIES OF FISSION PRODUCT LANTHANUM AND LANTHANIDES—I

ISOLATION OF TRACE LANTHANIDES USING NON-ISOTOPIC CARRIER AND DROP ELUTION TECHNIQUE

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Abstract—The use of lanthanum as a common carrier for all lanthanides has been studied. The results show that lanthanum under the given conditions carries trace lanthanum and lanthanides to the same extent. On this basis a radiochemical method for the determination of nuclear reaction yields has been developed. Lanthanum is used as carrier in fluoride and hydroxide precipitations for group isolation of all the lanthanides which are formed. A further group purification is obtained by an anion exchange step. The elements are thereafter separated from each other by cation exchange chromatography using ammonium lactate as eluant. The use of the non-isotopic carrier makes possible yield measurements of short-lived nuclides. The time needed is about one-tenth of that of previous methods. The fission yields obtained show a high degree of reliability. This is partly due to the weightless sources obtained, which considerably simplify measurements of absolute disintegration rates. Only a single chemical yield determination, that of the lanthanum, is sufficient to determine the recovery of all the lanthanides concerned.

Using this method improved half-lives are given for some nuclides in the lanthanum series: 3·87 ± 0·04 hr ^{141}La, 5·88 ± 0·10 hr ^{145}Pr, 11·14 ± 0·06 day ^{147}Nd, and 9·1 ± 0·7 hr ^{156}Sm. Two new neutron rich isotopes of terbium have been found to occur among the products of high energy induced fission with half-lives 6·5 ± 0·3 hr and 23 ± 2 hr. The probable mass numbers, based on fission yield measurements, are 163 and 164, respectively.

Vol.
15
1960

RADIOCHEMICAL determinations of fission yields are based on the knowledge of the chemical yields involved in the isolation of the elements of interest. As only trace amounts of the products are present in laboratory experiments it is necessary to add isotopic carriers prior to the chemical separations.

Concerning the elements in the lanthanum series* these are first isolated as a group while the separation of the elements from each other is subsequently performed by the ion-exchange adsorption-elution method. The degree and speed of the separation depend on many factors (e.g. column dimensions, resin, eluting agent, pH, flow rate, temperature etc.) but is strongly influenced by the amounts of carriers present.

The use of carriers is ordinarily avoided when short-lived nuclides are to be studied. When reaction yields are not required, excellent separations can be achieved by using small columns, very fine resin particles, high flow rate and elevated temperature, as in the methods developed by THOMPSON *et al.*[2] and by STEWART[3].

* In this paper the nomenclature decided by the International Union of Pure and Applied Chemistry for the elements nos. 57–71 is adopted,[1] i.e. *Lanthanum series* for the elements *La to Lu* inclusive, *and lanthanides—Ln*—for the elements *Ce to Lu* inclusive.

[1] *International Union of Pure and Applied Chemistry*: *Nomenclature of Inorganic Chemistry* p. 6. Butterworths, London (1959).
[2] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 6229 (1954).
[3] D. C. STEWART, *Analyt. Chem* **27**, 1279 (1955).

The separation of trace amounts can then be performed within a few hours and this time may be reduced according to the number of elements present.

The necessity of using isotopic carriers of several elements in fission yield determinations of lanthanum and the lanthanides leads, however, to a broadening of the elution bands compared with those obtained in the separation of only trace amounts.

To obtain adequate separations of neighbouring elements large columns are therefore required; these lead to much slower separations so that more than 10 hr are needed for the elution of only the lighter lanthanides.[4,5,6]

In order to reduce this inevitable effect of the carriers a recommended procedure is to load the column with carriers for one, or at most a few, of the elements of interest. Thus no carriers are added for elements adjacent to the one whose isotopes are selected for fission yield determinations. In this way only a very limited number of nuclides can be studied in each run and a freshly prepared fission mixture is often required for the majority of the runs. Consequently in order to cover all nuclides of interest this method gets very tedious.

With the increasing study of nuclear reactions development of a fast radiochemical method for determination of yields of nuclides in the lanthanum series based on the separation of trace amounts without the use of carriers has become a major requirement.

From the properties of the elements concerned one might expect that a carrier isotopic with only a single lanthanide product will act as collector for all. If it can be made to carry all the products to the same degree in a group separation and if the subsequent separation of the trace elements from each other could be performed without loss, then nuclear reaction yields of lanthanum and lanthanides (including promethium) could be measured in a single run.

Further advantages would include: a single chemical yield determination (the carrier element only) and a much more precise determination of disintegration rates in the final samples than in previous work. The latter becomes possible because the effects of self-absorption and self-scattering of β-particles are negligible in essentially weightless sources.

The general applicability of a fast radiochemical method for isolation and yield measurements based on the ideas just outlined is obvious. The present investigation is moreover justified by the importance of fission yields of nuclides in the lanthanum series.

Due to the difficulties emphasized above radiochemical fission yield measurements are very scarce and mostly performed in a laborious manner. The great majority of the available fission yields are therefore based on mass-spectrometric determinations. The results obtained, however, by different groups very often show large inexplicable discrepancies.

Development of a good radiochemical method would allow an independent and decisive check on the mass-spectrometric values. Moreover, the great advantage of a fast method would be that it might permit both cumulative and primary yield measurements thus giving promise of further progress in our understanding of nuclear fission.

[4] L. R. Bunney, E. C. Freiling, L. D. McIsaac and E. M. Scadden, *Nucleonics* **15**, No. 2, 81 (1957).
[5] J. G. Cunninghame, M. L. Sizeland, H. H. Willes, J. Eskins and E. R. Mercer, *J. Inorg. Nucl. Chem.* **1**, 163 (1955).
[6] W. E. Nervik, Report UCRL-4411 (1954).

CARRYING PROPERTIES OF LANTHANUM

The influence of carriers on the elution curve was studied using 1·0 mg of carrier isotopic with the relevant lanthanide. It was found that the width of the corresponding elution peak at half maximum increased about 100 per cent relative to that without carrier. It is, however, well established that the elution of the elements in the lanthanum series from a loaded cation exchange resin column will start with the heaviest one and be followed by the others in order of decreasing atomic number. It should therefore be expected that the presence of lanthanum carrier will not disturb the separation of trace amounts of the lanthanides from each other but only causes broadening and tailing of the lanthanum peak itself. This was verified experimentally as shown in Fig. 1. Accordingly 1·0 mg of lanthanum was chosen as a suitable carrier for all the lanthanides under the conditions described later.

The carrying properties of lanthanum for other elements cannot be predicted in detail. Earlier studies, however, of co-precipitation of trace amounts of other elements with a non isotopic carrier (mainly the radium–barium system) give some general indications.[7] Even if these co-precipitation results refer to equilibrium conditions their results should be relevant to the present case. Accordingly, as the elements in the lanthanum series show close similarities in chemical behaviour and crystal chemical properties, one would expect that trace amounts of the lanthanides will be carried by incorporation in the crystal lattice of the lanthanum precipitate. This is supported by studies of the ability of lanthanum to form mixed fluoride crystals with lanthanides. SCHYLER[8] has shown that these fluorides form solid solutions which extend from pure lanthanum fluoride to some upper value of the mole ratio Ln/(Ln + La). The latter decreases with increasing difference in ionic radii of the participating ions, but is always many orders of magnitude greater than can be anticipated in studies of the present type. These results prove that a small replacement of lanthanum by lanthanides can be tolerated in the lattice. The extent of co-precipitation of small amounts ought therefore to be independent of the particular lanthanide when fluoride precipitations are considered.

The other factors involved in the carrying process (lattice and hydration energies, etc.) are probably also very similar among these elements, while the solubilities for a given type of compound (e.g. hydroxides) may differ. One cannot, however, extrapolate from the solubility ratios to the distribution coefficient even if an approximate parallelism may be observed.[7] Within the crystal lattice there may be forces that decrease the influence of the absolute solubilities.

In the present work the determination of chemical yields of the various lanthanides participating in a group separation will be based entirely on the recovery yield of the lanthanum carrier. In view of this fact it is of major importance to obtain a clearer insight into the properties of lanthanum as a carrier for lanthanides on precipitates obtained by conventional lanthanum and lanthanide chemistry. Thus it is necessary to find out if trace lanthanides are carried to the same extent by lanthanum and if this is the case, how large a fraction of lanthanides is carried.

EXPERIMENTAL

A group separation of the elements in the lanthanum series should preferably be based on fluoride or hydroxide precipitations, or on both. A detailed study, however, of co-precipitation including

[7] O. HAHN, *Applied Radiochemistry* Chap. IV. Cornell University Press, Ithaca (1936).
[8] K. SCHYLER, *Arkiv för Kemi* **5**, 61 (1953).

Vol. 15 1960

homogeneous and heterogeneous distributions as obtained in equilbrium conditions, is outside the scope of the present work. Therefore the following simplified procedure was applied.

Test solutions of 1·0 mg lanthanum nitrate were added one of the following representative lanthanides in trace concentrations: 285 day ^{144}Ce*, 11·1 day ^{147}Nd, 2·64 year ^{147}Pm, 12·7 year ^{152}Eu + 16 year ^{154}Eu, and 72·3 day ^{160}Tb. The 40·22 hr ^{140}La was used as an indicator for the amount of lanthanum precipitated.

Zirconium hold-back carrier was added to the solutions which were made 2 M in nitric acid and 4 M in hydrcfluoric acid. The precipitations were performed at room temperature and addition of a few drops of acetic acid causes coarsening of the fluoride precipitate. The precipitate was washed with 1 M solution of ammonium nitrate and then dissolved by treatment with concentrated nitric acid and a saturated solution of boric acid. After a second fluoride precipitation and centrifugation aliquots of the supernatants and of the dissolved precipitates were evaporated to dryness in small

TABLE 1.—CARRYING OF TRACE LANTHANIDES ON LANTHANUM BY FLUORIDE PRECIPITATION†

Tracer	% carried relative to La	
^{147}Nd	99·7 100·1	99·9
^{152,154}Eu	100·2 100·3	100·3
^{160}Tb	100·3 99·8	100·1

TABLE 2.—CARRYING OF TRACE LANTHANIDES ON LANTHANUM BY HYDROXIDE PRECIPITATION†

Tracer	% carried relative to La	
^{144}Ce	100·2 100·2	100·2
^{147}Pm	100·1 98·5	99·3

counting cups under a heating lamp. The activities were measured by an end-window Geiger–Mueller counter. By following the decay of ^{140}La, the ratio of lanthanum to lanthanide is obtained.

In a parallel set of experiments the lanthanum in the test solution together with the appropriate trace lanthanide was precipitated twice as hydroxide with concentrated ammonium hydroxide solution. The degree of co-precipitation in these experiments was determined by comparing the activity of lanthanum and lanthanide in an aliquot of the test solution with that of the solution obtained by dissolving the second lanthanum hydroxide precipitate in dilute nitric acid. The counting of these samples were performed in a similar way to the fluoride studies above.

RESULTS

The results are summarized in Tables 1 and 2, and show that there is no measureable difference between the loss of lanthanum and of lanthanide activities. Thus it is found that under the present conditions the fraction of trace lanthanide incorporated in the lanthanum carrier is the same for each lanthanide and equal to the fraction of

* In equilibrium with 17·3 min ^{144}Pr.
† Tracer concentration $< 10^{-12}$ molar. Carrier concentration $\sim 2{\cdot}5 \times 10^{-3}$ molar.

lanthanum precipitated. In other words within the experimental uncertainties (estimated in Tables 1 and 2 at 2 per cent) one finds:

$$\frac{\text{Lanthanide in precipitate}}{\text{Lanthanum in precipitate}} = K \frac{\text{Lanthanide in solution}}{\text{Lanthanum in solution}}$$

where the distribution coefficient K can be set equal to unity for the co-precipitation of lanthanides in trace amounts with lanthanum carrier. Consequently these experiments show that lanthanum can be used safely as a carrier for the lanthanides in group separations based on fluoride and hydroxide precipitations.*

FISSION YIELD DETERMINATION OF LANTHANIDES USING NON ISOTOPIC CARRIER

Group isolation of the elements in the lanthanum series

A fluoride precipitation is usually applied as a group separation of the rare earths from the fission mixture. In order to avoid contamination by zirconium activities the fluorides are repeatedly precipitated from an acid solution always in the presence of zirconium hold-back carrier. In this way the rare earth fluorides are purified from zirconium activities. Co-precipitation of a small part of the hold-back carrier is not, however, easily avoided, and proves to be large enough to disturb the determination of the percentage recovery of the lanthanum carrier by the spectrophotometric method outlined later in this paper.

Lanthanum fluoride, however, may be precipitated without adding zirconium hold-back carrier. Athough the zirconium activities will then follow the lanthanum almost completely a separation should be expected in a later step, i.e. in the cation exchange column separation. In the latter zirconium is ordinarily eluted in front of yttrium and the lanthanides of interest when using ammonium lactate as eluting agent. Attempts to confirm this in the present case did not succeed, however, as fission product zirconium is converted to a radiocolloid during the treatment previous to the ion exchange step and the colloid interferes with the exchange separation.

As shown by KRAUS and NELSON[9] uranium and the majority of the fission products are adsorbed on a Dowex-1 anion exchange resin from a strong hydrochloric acid, while alkalis, alkaline earths, yttrium, lanthanum and lanthanides pass through†.

These observations were confirmed and the introduction of an anion exchange step after the fluoride precipitation (performed without zirconium hold-back carrier) eliminated completely the troubles caused by zirconium.

Tests had to be performed, however, on the behaviour of the trace lanthanides with respect to the lanthanum carrier when passing through the small anion exchange column described later.

The possible loss and discrimination between lanthanide activities was measured as follows: 0·500 ml of a test solution 8 M in hydrochloric acid containing 1·0 mg lanthanum carrier and the lanthanide tracers was passed through the column in 15 sec, whereafter this was washed with 0·5 ml 8 M hydrochloric acid. The eluate was adjusted to 1·000 ml. Aliquots were withdrawn from the original test solution and from the eluate, pipetted onto Scotch tape and the activities measured after evaporation to dryness under a heating lamp.

* A more detailed study of the co-precipitation of lanthanides on lanthanum compounds is now being undertaken.

† Ag (I), As (V), Br^- and Rh (III) will also appear in the eluate.

[9] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 113. United Nations, New York (1956).

Vol. 15 1960

The results are given in Table 3 and show that within the uncertainties in the measurements, the activity ratio of lanthanide to lanthanum is unchanged by introducing this purification step.

The next step in the group separation is the precipitation of the lanthanum carrier as hydroxide, which has already been proved to carry the lanthanides satisfactorily.

TABLE 3.—THE EFFICIENCY OF LANTHANUM AS CARRIER OF TRACE LANTHANIDES THROUGH AN ANION EXCHANGE COLUMN*

Tracer	Recovery in 1 ml eluate (%)	% carried relative to La
^{140}La	94·7 ± 2·4	101·8 ± 3·3
^{144}Ce	96·4 ± 2·2	
^{140}La	87·1 ± 0·7	101·8 ± 2·2
^{147}Pm	88·6 ± 1·0	

* Column: 3·4 mm in diameter, 23 mm long
Resin: Dowex-1 X2%, 200–400 mesh
Eluting agent: 8 M HCl

Separation of the lanthanides from each other

This is performed in the cation exchange step described later. The eventual loss associated with this step was determined by comparing the lanthanide activity of the test solution with the total activity found in the corresponding elution peak.

The loss was found to be 0·6 ± 0·4 per cent. Thus while the lanthanum activity will be quantitatively carried down the column with the stable lanthanum, the lanthanides are also washed down quantitatively in a carrier free state. The apparent 0–1 per cent loss is explained by the tailing of the elution peaks.

According to the results of these experiments it is very easy to determine the chemical yield of all the elements concerned. The content of lanthanum is measured in an aliquot withdrawn from the solution after the group isolation, but prior to the separation of the elements from each other. Thus the chemical yield of lanthanum is obtained and at the same time the chemical yields of the individual lanthanides.

Procedure. The procedure finally developed is the following one in which the group isolation can easily be performed in 15 min and the separation of the lanthanides from each other in less than an hour.

The irradiated uranium trioxide or uranium nitrate hexahydrate target is dissolved in 3–5 ml 2 M nitric acid containing 1·00 ml of carrier solution of lanthanum (~1 mg La) and 2·00 mg barium or strontium carrier depending on which is selected as fission monitor. Three drops of acetic acid is added and lanthanum fluoride precipitated by making the solution 4 M in hydrofluoric acid. The fission monitors (Ba resp. Sr) are later isolated from the supernatant liquid.

After washing with 5 ml M solution of ammonium nitrate the lanthanum fluoride is dissolved in three drops of boric acid (saturated solution) and eight drops of concentrated hydrochloric acid. The solution is transferred to the top of an anion exchange column 3·4 mm by 2·3 cm, packed with Dowex-1, 2 per cent crosslinked, 200–400 mesh resin particles. The lanthanum and the lanthanide activities are washed through by 0·75 ml 8 M hydrochloric acid. The eluate is evaporated almost to dryness to expel hydrochloric acid. After diluting in water the lanthanum hydroxide is precipitated twice using concentrated solution of ammonium hydroxide. The pure hydroxide is converted to chloride and dissolved in about 0·5 ml of 0·05 M hydrochloric acid. The latter should be freshly boiled to expel all air in order to prevent formation of air bubbles in the heated column during the

succeeding cation exchange step. It has been verified that no measurable amounts of other fission product activities except yttrium are present at this stage.

The apparatus for the separation of the rare earths from each other is a column of similar type to that described by THOMPSON *et al.*[12] The resin Dowex-50, 12 per cent crosslinked, "collodial" mesh was used after a fractionation of the particle size and a purification.

The resin bed is 2·0 mm in diameter with the height adjusted to 5 cm and has a free volume of 0·1 ml, about three drops. In order to attain equilibrium quickly between resin and solution a hot column is used. Trichlorethylene vapour maintains the column and the eluant at a temperature of 87 C.

Repurified lactic acid was used as eluant in a 0·4 M solution adjusted to pH 4·2 by ammonium hydroxide. To obtain optimal conditions the column is preconditioned by the warm eluant for several hours before use during which time the flow rate is slowed down to one drop about each 5 min. The lactate solution above the resin bed is then removed and the glass wall rinsed twice with boiled distilled water and twice with 0·05 M hydrochloric acid. Finally two drops of the latter is forced down the column.

From the 0·5 ml solution of the purified lanthanum and lanthanide activities known volumes (0·050 or 0·100 ml) are withdrawn, transferred to the column and the elements adsorbed on the top of the resin bed. The micropipettes are washed with 0·05 M hydrochloric acid and distilled water which are used to rinse the activities down the glass wall. A final rinsing is done with hot ammonium lactate solution and then elution starts.

The flow rate through the resin in the present work was adjusted by the height of the eluant container. The elution rate obtained by a water pressure of about 1·3 m was 1·0 ml/cm² per min, corresponding to one drop per min (0·032 ml per drop). The first drop leaving the column after the eluant started moving down the resin bed was selected as drop number one.

Preparation of resin and eluant. The fractionation of the Dowex-50, 12 per cent crosslinked, "collodial" mesh can adequately be done by sedimentation in glass cylinders containing 1 M nitric acid.[10] Particles with settling rate 2·5–5·0 mm per min are separated by decantation of suspended resin from the cylinder and are found to be 15–30 μ in diameter. This fraction is washed with a 2 M solution of ammonium thiocyanate in order to remove iron, then three times with distilled water, alternated with a 6 M hydrochloric acid and a 6 M ammonium hydroxide wash. The purified resin is transferred to the column as a suspension in boiling distilled water.

The lactic acid solution used in the eluant was prepared from Riedel de Häen A/G DAB 6 grade. An analysis, however, disclosed the presence of contaminating cations (150 p.p.m. in the undiluted acid). These were mainly calcium and magnesium but their presence would result in bad separations.[2] The alkaline earths are removed by passing the lactate solution through an cation exchange column, 12 mm by 10 cm, loaded with Dowex-50, 12 per cent crosslinked, 200–400 mesh resin in hydrogen form. The purified acid is adjusted to pH 4·2 by ammonium hydroxide using a Beckman pH meter and diluted to 0·4 M in lactate. Finally a small amount of phenol (0·01 M) is added to prevent formation of microorganisms.

Counting techniques. Since the gross activity of the elements separated in the ion exchange step has to be established, each drop leaving the column must be prepared for counting. A turntable of Perspex, 40 cm in diameter, covered with asbestos sheet was placed under the column. It rotated continuously at a rate of about one turn per hour. Two pieces of semi-circular aluminium foils of thickness 2·4 mg/cm² were placed on the turntable to collect the falling drops. The distance between these was about 2·5 cm on the foil. The drops passed two infra-red lamps in succession, their heights above the foil being regulated to evaporate the water and the lactate respectively and to leave no residue of solid matter only a small brown mark for visual identification. Strips 12–13 mm broad were cut from the foils and fastened by adhesive to standard punched counting cards with the sample in the centre.

The samples were counted with an end window Geiger–Mueller tube (TGC-2) in a standard counting arrangement, following the techniques of absolute counting necessary to convert the observed activities to absolute β-distintegration rates.[11]

The samples prepared by the present method are essentially weightless, on thin backing material

[10] J. P. SURLS, JR., Report UCRL–3209 (1956).
[11] A. C. PAPPAS, Report AECU–2806, MIT-LNS-63, (Part II) E and F (1953); (Inaugural Dissertation, University of Oslo).

Vol. 15 1960

(2·4 mg/cm² Al) and do not need any cover. This increases the accuracy of and simplifies the calculation of absolute disintegration rates, because the uncertain estimation of the self-absorption and self-scattering in thick samples is avoided.

In the present case the absolute disintegration rate is related to the observed activity as follows[11]

$$\frac{\text{observed activity}}{\text{absolute disintegration rate}} = G f_B f_W f_A f_R f_B f_S \qquad (1)$$

where:

G = geometry factor

f_B = counting efficiency calculated as:

[nos. of β-particles per decay + 0·01 × E^γ (MeV) × nos. of γ per decay] for $E^\gamma > 0{\cdot}4$ MeV

In the low geometry used (~3 per cent) the number of coincidences are small and can be neglected. The absorption factor f_W, and the backscattering factor f_B are given in the published literature.[11,12]

The factors f_S for self-absorption and self-scattering are in the present work both equal to unity as a result of the way the samples are prepared.

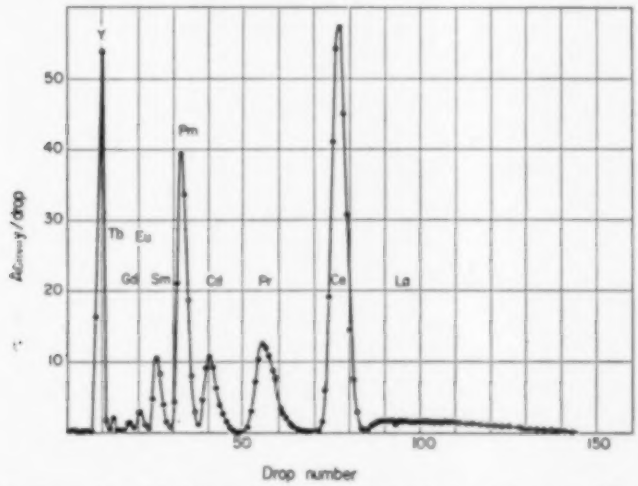

FIG. 1.—Separation of fission product rare earths (yttrium and elements of the lanthanum series) by ion exchange column.

Column dimensions: 2 mm by 5 cm, resin Dowex-50 × 12 per cent, collodial, eluting agent 0·4 M ammonium lactate, pH 4·2, temperature 87° and flow rate one drop per min.

Determination of individual nuclides. Each sample was first counted for about half a minute and the elution curve drawn (Fig. 1) in order to identify each element.*

By adding the activities of the drops under the same elution peak the total peak activity A_P of all isotopes present of a single lanthanide is established. This determination was usually very accurate because: the counting time was sufficient to give good statistics for the total activity, 0·5–2 per cent standard deviation depending on the fission yield involved. Furthermore the time elapsed between the counting of the first and the last drop belonging to the same lanthanide peak was very short compared to the half-lives of the nuclide involved. Thus the error introduced by this time difference is negligible. In lanthanum, i.e. 3·9 hr ^{141}La, however, the broadening of the peak caused by the carrier results in a ratio of total counting time to half-life of about 0·4. This value gives rise to an error in A_P of less than 0·5 per cent.[11]

* The positions of the different lanthanides and lanthanum in the elution curve were determined in separate runs by means of radioactive tracers.

[12] G. RUDSTAM, *Spallation of Medium Weight Elements* Chap. 1F. *Inaugural Dissertation*, University of Uppsala (1956).

The decay of the activity of one drop at the top of the elution peak is followed. Analysis of the gross decay curve discloses the different isotopes of the particular element present and their contribution to the total activity A of this sample. If the activities of these isotopes are $a_1, a_2 \ldots a_i \ldots a_n$ when referred to the time of measurement of the total peak activity then the total activity of the i'th isotope of the element concerned is given by:

$$A_i = A_P \frac{a_i}{A} \tag{2}$$

Determination of chemical yield. The chemical yield of the lanthanum carrier and thereby of all the lanthanide nuclides involved is measured in aliquots withdrawn from the 0·5 ml solution obtained after the group separation. The small quantities of lanthanum involved (1 mg carrier added) require

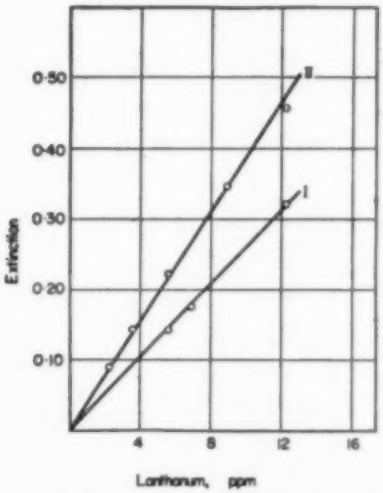

FIG. 2.—Determination of lanthanum as alizarin sulphonate in an aqueous solution (I) and in 60 per cent water–40 per cent acetone solution (II).
Both are buffered with acetic acid and ammonium acetate.

a micro-analytical method for their determination. The colorimetric method developed by KOLTHOFF and ELMQUIST[13] using sodium alizarin sulphonate as complexing agent was adapted. The optical density of the solution is measured at 520 mμ using a Beckman quartz spectrophotometer Model DU. With 1 cm cuvettes, however, the optical density is too low to obtain results of the desired accuracy, i.e. 1–2 per cent uncertainty. It is known that linear absorption holds up to about 12 mg lanthanum per 1000 ml, but an optimal light transmission is not obtained. WOODS and MELLON[14] were, however, able to increase the sensitivity of the determination of iron as its thiocyanate complex by adding acetone to the solution. Trying this artifice in the present case a marked increase in the optical density is obtained. Using a solution with 40 per cent acetone the increase in the extinction is about 50 per cent of that of a pure aqueous solution (Fig. 2).

Calculation of fission yields. The cumulative fission yields of nuclides with short-lived parents and the independent fission yields of shielded nuclides are easily calculated from their absolute disintegration rates, their chemical yield, and the corresponding data for the fission monitor.[15]

The half-lives involved in parent–daughter relationships are sometimes of such magnitudes that parent and daughter activities may simultaneously be found in adjacent peaks of the elution curve (the daughter preceding the parent). In such cases it is possible to measure cumulative yield of the parent besides the independent yield of the daughter. In order to succeed, however, the observed

[13] I. M. KOLTHOFF and R. ELMQUIST, *J. Amer. Chem. Soc.* **53**, 1217 (1931).
[14] Y. T. WOODS and M. G. MELLON, *Industr. Engng. Chem. (Analyt.)* **13**, 551 (1941).
[15] A. C. PAPPAS, Report AECU–2806, MIT-LNS-63, Part II, H (1953).

Vol. 15 1960

daughter activity must be corrected for the amount grown from the parent previous to the separation from each other.

The disintegration rate $(D_B)_t$ of the daughter B at a separation time t (after the end of the irradiation) from the parent A gives an apparent yield $(Y_B)_t$ of the daughter.[15]

$$(Y_B)_t = \frac{1}{R} \frac{1}{(1 - e^{-\lambda_B T}) e^{-\lambda_B t}} \tag{3}$$

where R the fission rate is known through the fission monitor; T is the irradiation time.

The measured disintegration rate of the daughter at time t consists, however, of the disintegration rate of the amount formed independently $(D_B^c)_t$ and the amount formed by decay of the parent during $(D_B^A)_T$ and subsequent $(D_B^A)_t$ to the irradiation:

$$(D_B)_t = (D_B^c)_t + (D_B^A)_T + (D_B^A)_t \tag{4}$$

The general expression in reference (15) gives:

$$(D_B)_t = \frac{R(Y_A^c)}{\lambda_A - \lambda_B} [\lambda_A(1 - e^{-\lambda_B T}) e^{-\lambda_B t} - \lambda_B(1 - e^{-\lambda_A T}) e^{-\lambda_A t}] + R(Y_B^c)(1 - e^{-\lambda_B T}) e^{-\lambda_B t} \tag{5}$$

where (Y_A^c) and (Y_B^c) denote the cumulative yield of the parent and the independent yield of the daughter, respectively.

According to equation (3) the apparent yield is

$$(Y_B)_t = \frac{(Y_A^c)}{\lambda_A - \lambda_B} \left[\lambda_A - \lambda_B \frac{(1 - e^{-\lambda_A t}) e^{-\lambda_A t}}{(1 - e^{-\lambda_B t}) e^{-\lambda_B t}}\right] + (Y_B^c) \tag{6}$$

The independent yield of the daughter:

$$(Y_B^c) = (Y_B)_t - (Y_A^c) \frac{\lambda_A}{\lambda_A - \lambda_B} \left[1 - \frac{\lambda_B}{\lambda_A} \frac{1 - e^{-\lambda_A T}}{1 - e^{-\lambda_B T}} e^{-(\lambda_A - \lambda_B)t}\right] \tag{7}$$

can thus be computed from its apparent yield and the cumulative yield of the parent. (The latter is determined by studying the elution peak of the parent element.)

When using short irradiation times compared to the half-lives involved equation (7) reduces to

$$(Y_B^c) = (Y_B)_t - (Y_A^c) \frac{\lambda_A}{\lambda_A - \lambda_B} [1 - e^{-(\lambda_A - \lambda_B)t}] \tag{8}$$

DISCUSSION AND RESULTS

It has been proved that the method developed in the preceding part of this paper does not introduce any systematic error. Moreover, the new method has many advantages compared with the standard isotopic carrier methods:[4–6]

(1) The time necessary for the separation and isolation of the lanthanides is of the order of one tenth of that previously used. Thus yield measurements of even short-lived nuclides are possible.

(2) A simplification in chemical yield determinations is obtained by the use of a single carrier for all the elements concerned.

(3) Compared with the usual radiochemical methods using weightable amounts of isotopic carriers the present method eliminates a serious source of error in the absolute counting procedure by making the effect of the sample thickness negligible*.

* The factor f_s in equation (1) for the effect of the sample thickness is by definition equal to unity for weightless sources in the relation (observed activity)/(absolute disintegration rate).

In this respect the present method is similar to the collector method developed by Rudstam[16].

(4) The use of expensive carriers are avoided,

(5) Yields of promethium isotopes are now measurable and obtainable with the same reliability as for the other lanthanide nuclides.

Precision of fission yield measurements

The application of the present method in fission yield studies of lanthanides from high energy proton and from thermal neutron induced fission of uranium will be the topic of succeeding papers in this series.

To illustrate, however, the precision (internal consistency) of fission yield measurements the standard deviation of a single determination is calculated from yield measurements of some lanthanide nuclides in fission of uranium induced by thermal (pile) neutrons.

On the basis of twelve determinations of the lightest nuclides (lanthanum, cerium and praseodymium) the mean standard deviation of a single determination was $\sigma =$ 2·4 per cent. Eight determinations of the heavier nuclides (neodymium and promethium) gave $\sigma = 7$ per cent. When all nuclides are determined from a single run as above, the counting errors are, however, larger for heavier than for lighter nuclides, due to the much lower (about three orders of magnitude) fission yields of the former ones as revealed from the well known yield mass curve. This accounts for the larger standard deviation in the obtained fission yields of the heavier nuclides in single run measurements.

In the fission of uranium induced by 170 MeV protons the yields in the lanthanides region do not decrease so rapidly with mass number as in thermal fission, $d \log Y/dA \sim -0{\cdot}10$ mbarns/mass number in the former compared to $-0{\cdot}35$ mbarns/mass number in the latter case. The determination of lanthanum and promethium yields are therefore performed simultaneously without ostensible difference in precision.

Vol. 15 1960

*Half-life determinations**

The half-life data of several lanthanum and lanthanide nuclides reported in the literature are often uncertain because of difficulties in preparing pure samples by fast chemical separations.

The elements isolated by the present method are obtained in a highly pure state as illustrated by the elution curve in Fig. 1. The samples made from the evaporated drops at the maximum of the elution peaks are specially suited for half-life determinations. The activities are very high and the decay can be followed during an unlimited length of time as the radioactive sources are not exposed to any material loss or geometrical displacement of the mounted samples.

The values obtained in the present work for some nuclides are given in Table 4 where the number of half-lives observed measures that part of the resolved gross decay curve which show a pure exponential decay of the nuclide of interest (Figs. 3–5).

Previous to this investigation the half-life of ^{141}La was reported to 3·5 hr[18]

* Some of the data given in this and the following section have been reported as preliminary data.[17]

[16] G. RUDSTAM, *Nucleonics* **13**, 64 (1955); Inaugural Dissertation, Chap. 1D. University of Uppsala (1956).
[17] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, Table of Isotopes, *Rev. Mod. Phys.* **30**, 585 (1958).
[18] O. HAHN and F. STRASSMANN, *Naturwissenchaften* **30**, 324 (1942).

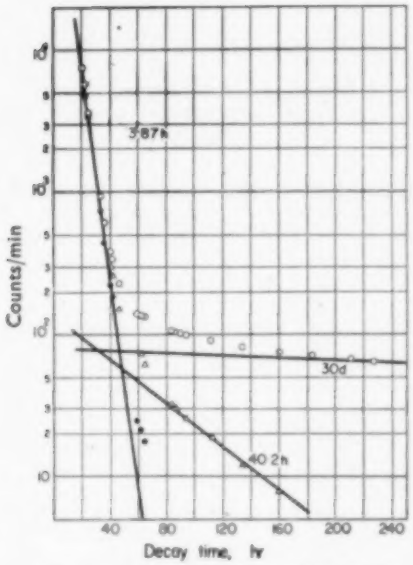

FIG. 3.—Analysis of decay of lanthanum activities from fission showing 3·87 hr ^{141}La, 40 hr ^{140}La and 30 day ^{141}Ce.
○ observed points.

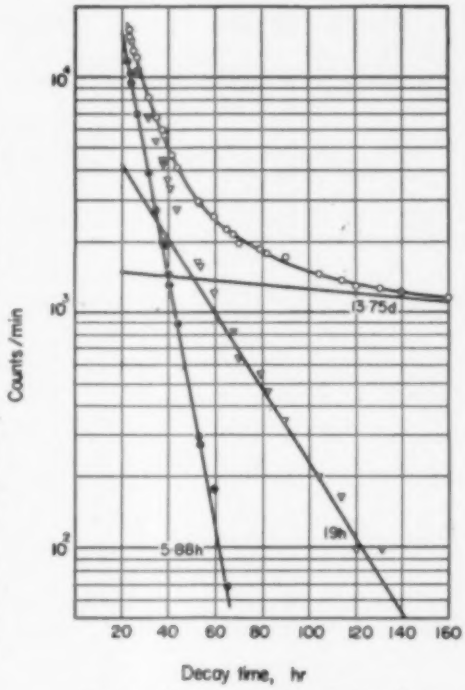

FIG. 4.—Analysis of decay of praseodymium activities from fission showing 5·88 hr ^{146}Pr, 19 hr ^{143}Pr and 13·75 day ^{143}Pr.
○ observed points.

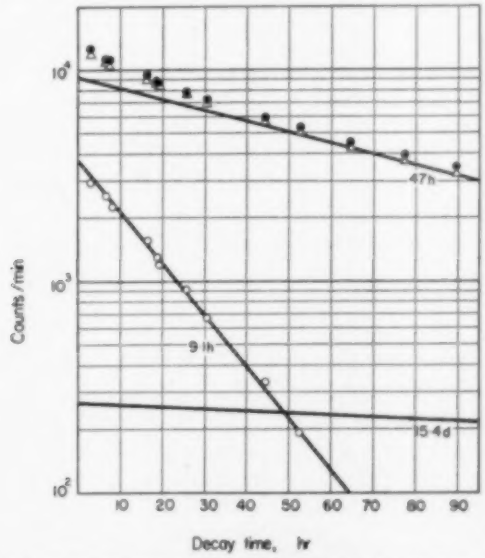

FIG. 5.—Analysis of early decay of samarium activities from fission showing 47 hr ^{153}Sm 9·1 hr ^{155}Sm and 15·4 day ^{156}Eu.
● observed points.

and 3·7 hr.[19] The half-life given in column 5 in Table 4 is 3·87 ± 0·04 hr. Compared with recent data only available to the authors after the present determination was accomplished this value is in excellent agreement with 3·85 ± 0·10 hr reported by SCHUMAN *et al.*[20] from lanthanum samples milked from purified fission product barium.

TABLE 4.—EXPERIMENTALLY DETERMINED HALF-LIVES OF LANTHANUM AND LANTHANIDE NUCLIDES

Nuclide	Sample no.	Number of half-lives observed in the decay followed	Half-life	
			Observed	Mean value and stand. dev.
^{141}La	1	3	3·90 hr	3·87 ± 0·04 hr
	2	5	3·88 hr	
	3	7·5	3·83 hr	
	4	7·5	3·94 hr	
	5	7	3·88 hr	
	6	7	3·80 hr	
^{143}Pr	1	5	5·80 hr	5·88 ± 0·10 hr
	2	7	5·80 hr	
	3	6	6·00 hr	
	4	8	5·75 hr	
	5	10	6·00 hr	
	6	7	5·95 hr	
^{147}Nd	1	2	11·25 days	11·14 ± 0·06 day*
	2	7	11·04 days	
	3	4·5	11·10 days	
	4	4	11·27 days	
	5	2·5	11·10 days	
	6	2	11·25 days	
	7	10	11·15 days	
^{156}Sm	1	2	10·0 hr	9·1 ± 0·7 hr
	2	3	9·5 hr	
	3	3	8·5 hr	
	4	3	8·3 hr	

* Weighted mean

By a fast isolation of fission product ^{145}Ce followed by a separation of ^{145}Pr MARKOWITZ *et al.*[21] found a half-life of 5·95 ± 0·10 hr for ^{145}Pr. This is higher than the value 5·88 ± 0·10 hr, given in Table 4, both determinations, however, agree within the uncertainties given. The most recent value 5·98 ± 0·02 hr given in a short note without details by DROPESKY *et al.*[22] is however, slightly higher than the value given in Table 4.

[19] S. KATCOFF, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN NNES, Plutonium Project Record, Div. IV, Vol. 9, Paper 172. McGraw-Hill, New York (1951).
[20] R. P. SCHUMAN, E. H. TURK and R. L. HEATH, *Bull. Amer. Phys. Soc.* **3**, No. 5, 315 (1958).
[21] S. S. MARKOWITZ, W. BERNSTEIN and S. KATCOFF, *Phys. Rev.* **93**, 178 (1954).
[22] B. J. DROPESKY, D. C. HOFFMAN and W. R. DANIELS, *Bull. Amer. Phys. Soc.* **4**, No. 1, 57 (1959).

Vol. 15 1960

Concerning the half-life of ^{147}Nd values in the region 11·0–11·9 days have been reported.[23–26]

The present value 11·14 ± 0·06 day and 11·06 ± 0·04 day given recently by WRIGHT *et al.*[27] are in substantial agreement.

Only an approximative value of about 10 hr for the half-life of ^{156}Sm is published.[28] The results of the present determination give a value of 9·1 ± 0·7 hr for this nuclide.

New radioactive isotopes of terbium

The terbium activity isolated from 170 MeV proton induced fission in uranium shows the occurrence of four components in the decay curve (Fig. 6). Besides a long

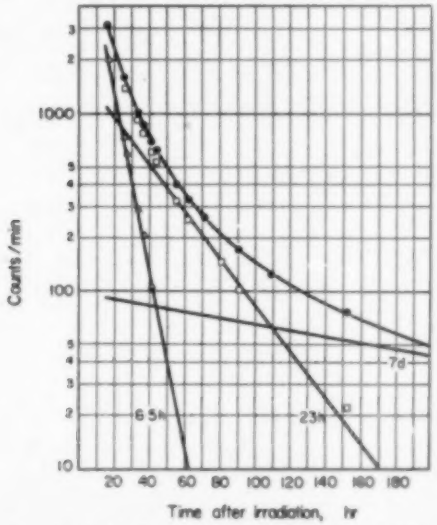

FIG. 6.—Analysis of early decay of terbium activities from fission showing components of 6·5 hr and 23 hr half-lives and 7 day ^{161}Tb.

lived activity attributed to the 72·3 day ^{160}Tb and the 7·0 day ^{161}Tb two more species are present, with half-lives 23 ± 2 hr and 6·5 ± 0·3 hr. The 23 hr component is still present in the terbium peak when elution is performed after the 6·5 hr activity has decayed away. As furthermore the 6·5 hr activity does not grow from the 23 hr species (conf. Fig. 6) one can conclude that there exsists no parent daughter relationship between these two species. These are thus chemically proved to be isotopes of terbium and it remains to assign their mass numbers.

[23] J. A. MARINSKY and L. E. GLENDENIN, *Radiochemical Studies: The Fisson Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, Paper 191. McGraw-Hill, New York (1951).
[24] W. S. EMERICH and J. B. KURBATOV, *Phys. Rev.* **83**, 40 (1951).
[25] W. C. RUTLEDGE, J. M. CORC and S. B. BURSON, *Phys. Rev.* **86**, 775 (1952).
[26] E. KONDAIAH, *Phys. Rev.* **81**, 1056 (1951).
[27] H. W. WRIGHT, E. I. WYATT, S. A. REYNOLDS, W. S. LYON and T. H. HANDLEY, *Nucl. Sci. Engng.* **2**, 427 (1957).
[28] L. WINSBERG, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, Paper 198. McGraw-Hill, New York (1951).

Feather analysis of absorption curves in aluminium of the β-particles from a mixture of the two activities shows the presence of β-energy of about 2 MeV. Using the Bohr–Wheeler equation for ground to ground state decay energies in isobaric decay one finds using appropriate parameters[29] that there is no mass number just above 161 that can be excluded when searching for two isotopes of terbium. The yields, however, of the 6·5 hr Tb and the 23 hr Tb in the fission of uranium with 170 MeV protons* show that one gets the best fit to a smooth mass distribution curve if the mass numbers are 163 and 164, respectively. That the 6·5 hr Tb and the 23 hr Tb does not have mass number beyond 164 is also supported by the fact that no radioactive dysprosium daughters are observed in their decay. Thus it is very likely that the new isotopes are ^{163}Tb and ^{164}Tb with half-lives 6·5 $\pm$ 0·3 hr and 23 $\pm$ 2 hr, respectively.

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The authors are indebted to the Royal Norwegian Council for Scientific and Industrial Research for financial support.

* Succeeding paper in this series.

[29] R. A. BRIGHTSEN, C. D. CORYELL and A. C. PAPPAS, see C. D. CORYELL, *Ann. Rev. Nucl. Sci.* **2**, 305 (1953).

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 237 to 241. Pergamon Press Ltd.

ON THE ELECTRONEGATIVITIES OF THE GROUP IV ELEMENTS

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Abstract—Reported values for the electronegativities of the Group IV elements are critically reviewed and it is concluded that the electronegativities of Si, Ge, Sn and Pb are essentially constant or decrease slightly. It is further concluded that in contrast to a previous suggestion, the electronegativity differences have essentially no effect upon the chemistry of these elements, and cannot be correlated with either the nuclear quadrupole coupling of the tetrahalides or the chemical shift of the alkyl derivatives.

THE concept of electronegativity is one which has been of some value to the inorganic chemist. The excellent review article by PRITCHARD and SKINNER[1] contains some applications and summarizes the various methods used to calculate electronegativities. In general, the electronegativity values obtained by the various methods are in reasonably good agreement.

Recently, the electronegativities of the Group IV elements have been re-evaluated[2] by ALLRED and ROCHOW. For lead, a large discrepancy was observed in the electronegativity values obtained by the different methods employed by these authors. A reason for this discrepancy will be offered and in so doing a weakness in the thermodynamic method for obtaining electronegativities will be emphasized.

Arguments will be presented to support the conclusion that the electronegativities of Si, Ge, Sn and Pb are essentially constant (or decrease slightly) and, in contrast to a previous suggestion,[2] differences most probably are insignificant in explaining the chemistry of the compounds of these elements.

In an earlier publication,[3] the importance of orbital overlap in explaining the stabilities of the Group IV halides was demonstrated. It was shown that the bond between lead and chlorine is much weaker than the bond between chlorine and other Group IV elements. This is explained by having less efficient overlap between the chlorine and the diffuse lead orbital than there is with the smaller elements. An additional effect is the repulsion of chlorine non-bonding electrons with the non-bonding electrons of the Group IV element. This effect leads to bond weakening for many Ge and Pb compounds. A similar argument will be employed to reinterpret the data discussed by ALLRED and ROCHOW on the nuclear quadrupole resonance of the tetrachlorides and on the chemical shift of the alkyl derivatives of the Group IV elements.

DISCUSSION

It is difficult to define the concept of electronegativity. However, in order to

[1] H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1954).
[2] A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 269 (1958).
[3] R. S. DRAGO, *J. Phys. Chem.* **62**, 353 (1958).

prevent this from being an empirical reactivity constant without any physical significance a definition is necessary. In valence bond terminology the actual bond ψ_0, between atoms A and B is represented as a resonance hybrid of the extreme forms:

$$\psi_0 = \gamma_1\psi A^+B^- + \gamma_2\psi A^-B^+ + \gamma_3\psi A^-B \quad (1)$$

where the γ's are the mixing coefficients that designate the contribution of each form. If $\gamma_1 > \gamma_2$, B is more electronegative and if $\gamma_2 > \gamma_1$, A is more electronegative.

Thus, electronegativity is a measure of the tendency of an atom to displace the electron density involved in bonding away from the other atom. A large nuclear attraction for the bonding electrons is the essence of a large electronegativity.* In view of these considerations, the "new[2] set of electronegativities" C = 2·6, Si = 1·9, Ge = 2·0, Sn = 1·9 and Pb = 2·5, is particularly disturbing. Lead, the larger element with the smaller ionization potential, is more electronegative than silicon. The following paradox arises: The more electronegative element lead is more metallic in its properties and reactions than the less electronegative element silicon. There is obviously something wrong.

In an attempt to gain a measure of the nuclear attraction for the bonding electrons, MULLIKEN[4] proposed a relationship between electronegativity and the average of the ionization potential and electron affinity. Although the electron affinity of lead is not accurately known, a reasonable estimate gives lead a smaller electronegativity value than silicon. The series then becomes C $\gg$ Si > Ge $\approx$ Sn $\approx$ Pb. Electronegativity values based upon the stretching force constants[5] of the bond determined spectroscopically produce the series C $\gg$ Si > Ge $\approx$ Sn > Pb.

A high value is obtained for the electronegativity of lead by the thermochemical method. A brief review of this method is necessary before pointing out the source of error and thus establishing the low value for the electronegativity of lead.

The thermochemical evaluation has as its basis the postulate that the actual structure ψ_0 of the molecule A–B is lower in energy than the pure covalent structure ψA–B by an amount of energy due to ionic resonance. The following equation is used to calculate the ionic resonance energy:

$$\Delta = D(\text{A–B}) - \tfrac{1}{2}[D(\text{A–A}) + D(\text{B–B})] \quad (2)$$

where D(A–B) is the measured heat of dissociation of gaseous A–B, D(A–A) the heat of dissociation of A_2, D(B–B) of B_2 and $\frac{1}{2}[D(\text{A–A}) + D(\text{B–B})]$ is an approximation to the energy of the pure covalent structure ψA–B. Δ is then empirically related to the electronegativity difference $X_A - X_B$ by the expression:

$$X_A - X_B = 0{\cdot}208\sqrt{\Delta} \quad (3)$$

When A = Cl and $X_A = 3{\cdot}0$ it follows that a small Δ value gives rise to a large electronegativity for B.

An alternative approach to averaging the heats of dissociation to produce the pure covalent bond energy involves taking the geometric mean of $D_{(A-A)}$ and $D_{(B-B)}$, i.e. $\sqrt{(D_{(A-A)})(D_{(B-B)})}$. The values for Δ', calculated by employing the geometric mean are reported in Table 1 along with the resulting electronegativity X_B'. Since $D_{(Pb-Pb)}$

* For a more detailed discussion of electronegativity and for an explanation of the important concept of orbital electronegativity the reader is referred to the article by PRITCHARD and SKINNER[1].

[4] R. S. MULLIKEN, *J. Chem. Phys.* **3**, 573 (1935).
[5] W. GORDY, *J. Chem. Phys.* **14**, 305 (1946).

is not accurately known several assumed values have been employed. These data show that the largest source of error is introduced into the value by improper averaging and by lack of an accurate value for $D_{(Pb-Pb)}$. The estimate of the pure covalent bond energy for Pb—Cl is incorrectly given by averaging, for even with $D_{(Pb-Pb)} = 0$, the energy for the pure covalent bond is 29 kcal/mole. This is to be compared with a value of zero obtained by the geometric mean. High estimates of the pure covalent bond energy cause a small Δ value and a high electronegativity. Thus, for small values of $D_{(B-B)}$, averaging cannot be employed to give the pure covalent bond energy and values obtained by the geometric mean are very sensitive to errors in the value of $D_{(B-B)}$. For heavy elements, where $D_{(B-B)}$ is low electronegativities cannot be accurately obtained using equation (2) in any form.

TABLE 1.—EFFECT OF ERROR IN $D_{(B-B)}$ ON Δ AND Δ' VALUES

A = Cl B = Pb $D_{(A-A)}$ = 58 kcal/mole X_A = 3·0 $D_{(A-B)}$ = 58 kcal/mole

$D_{(B-B)}$ kcal/mole	Δ	X_B	Δ'	X_B'
25	16·8	2·2	20	2·1
15	21·8	2·0	29	1·9
0	29·3	1·9	58	1·4

TABLE 2.—ΔH°_{298} FOR THE REACTION:[3]

$MCl_4(g) \rightarrow M_{(g)} + 2Cl_2$

M	ΔH°_{298} kcal/mole
C	197·2
Si	233·7
Ge	200·3
Sn	192·7
Pb	115·2

There are additional effects contributing to the standard covalent bond energy that cannot be compensated for by averaging. There are good quantum mechanical arguments to support a decrease in covalent bond strength with increasing atomic number. As the atomic number increases in Group IV, the radial part of the wave-function changes in such a fashion as to make the orbitals larger. The larger orbital of lead overlaps less effectively with the smaller chlorine orbital than the silicon orbital does; so, less of the electron density of lead is involved in bonding and the bond is weaker. The values for the heat of dissociation of the Group IV tetrachlorides into the gaseous metal atom and the free halogen are reported in Table 2 and support this trend. The low value for carbon is consistent with a high electronegativity. An added effect of importance in the case of germanium and lead involves repulsion by the inner non-bonding electrons. The addition of the inner *d* electrons to germanium and the *f* electrons to lead places considerable electron density on both these elements. This increased electron density causes greater repulsion with the non-bonding electron density on chlorine and results in bond weakening as evidenced by the values in Table 2. (Note the large difference in Si vs. Ge and Sn vs. Pb.)*

* An alternative explanation invokes π-bonding. There is less π-bonding in Ge than in Si and less in Pb than in Sn because of the increased electron density on the elements Ge and Pb.

If these effects are not correctly compensated for in determining the normal covalent bond energy of Ge—Cl and Pb—Cl, the ionic resonance energy will be low and the electronegativity high. The averaging techniques employed to give the normal covalent bond energy do not adequately correct for these effects. Thus, the accuracy of the reported values is not as great as the difference. This shortcoming leads one to conclude that the best electronegativity values for the Group IV elements are C = 2·5–2·6; Si = 1·8–1·9; Ge = 1·8–1·9; Sn^{IV} = 1·8; Pb^{IV} = 1·8–1·7 and a limit of error of at least ±0·2 exists for Ge, Sn and Pb.

A brief discussion will be presented on the other phenomena discussed in the article by ALLRED and ROCHOW which in view of the above discussion were incorrectly attributed to electronegativity and can be reasonably interpreted in terms of overlap considerations and electron repulsions. This discussion will demonstrate that the phenomena to be discussed cannot be used to support an electronegativity scale.

The interpretation of the quadrupole coupling constants (eQq) of the halogen derivatives of the Group IV elements is a complex problem . In general, for the tetrahalides, the eQq values decrease in the order $CX_4 > GeX_4 > SnX_4 > SiX_4$. Since the eQq value for a halide ion is zero, ALLRED and ROCHOW interpreted the above sequence to indicate that the halogen is most ionic in SiX_4 and thus silicon is least electronegative.

An additional factor affecting the eQq value is the hybridization of the halogen. As the amount of *s* character increases in the hybrid orbital used by the halogen in bonding to the Group IV element, the eQq value also decreases. This effect was dismissed as an explanation by ALLRED and ROCHOW, but it can be demonstrated that it is an effect which is of importance in explaining the difference between the eQq values for SiX_4 and GeX_4. It has been shown[3] that a Si—Cl bond is about 8 kcal/mole stronger than a Ge—Cl bond. The chlorine will thus hybridize more to use the strongest bonding orbital (approaching *sp*) when it is bonded to silicon for larger overlap is obtained as *s* character is introduced into the halogen hybrid. As the bond to halogen becomes weaker, the halogen will employ a bonding orbital which has less *s* character in it and retain the lower energy *s* shell for a non-bonding pair of electrons. Since the Ge—Cl bond is weaker than the Si—Cl, it would have less *s* character and a correspondingly higher eQq value.

As indicated in a recent review article on this subject,[6] it is impossible to distinguish between changes in ionic character, *s* hybridization and π-bonding effects on the basis of only nuclear quadrupole results. It is almost certain that all of the above effects are operative and should be included in the complete interpretation of these results. In order to get a rough indication of the order of magnitude of the difference in "*s* character" of a chlorine bonded to silicon and germanium, one can assume no π-bonding and constant electronegativity for these two elements. About 10 per cent more "*s* character" is required in the chlorine bonded to silicon to account for the low quadrupole than is present in the chlorine bonded to germanium. Very little *s* hybridization occurs in the chlorine attached to germanium. The actual amount of "*s* character" in both these tetrahalides would have to be increased to compensate for any π-bonding.

The nuclear magnetic resonance results of the tetra-alkyls of the Group IV elements can be interpreted by employing the same arguments, assuming a slightly

[6] W. J. ORVILLE-THOMAS, *Quart. Rev.* **11**, 162–188 (1957).

Vol. 15 1960

decreasing electronegativity with increasing atomic number. As the strength of the bond to carbon varies for the different Group IV elements, the hybridization of the carbon varies. It is a known fact that the carbon-hydrogen angle (H—C—H) changes in molecules of the type CH_3—X as X is varied. It has recently been demonstrated that a change in hybridization follows the angle.[7] The weak bond between lead and carbon results in an increase in the amount of *s* character in the carbon hybrid orbital of the C—H bond. This increases the electronegativity of the carbon and removes electron density from the hydrogen making it less shielded. Thus, as the bond strength decreases in the series Si > Ge ≈ Sn > Pb, the chemical shift of the methyl group relative to water also decreases.[2] This indicates that the methyl groups attached to lead are least shielded.

Finally, it has been demonstrated[8] that it is foolhardy to attempt to correlate chemical behavoiur with any quantum mechanical phenomena without a complete knowledge of all the thermodynamic properties of the steps involved in the reaction.

The chemical properties of the Group IV elements discussed by ALLRED and ROCHOW are complex reactions and the energies corresponding to the various factors that could be affecting the reactions can not be obtained. Such information is available with regard to the stability of the chlorides of these elements and has been employed to explain their behaviour.[3] In the absence of such information on the oxides, imides, etc., no attempt will be made to explain their reactivities.

[7] M. KARPLUS and D. M. GRANT, *Proc. Natl. Acad. Sci.* **45**, 1269–73 (1959).
[8] F. G. A. STONE, *Chem. Rev.* **58**, 101 (1958).

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J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 242 to 249. Pergamon Press Ltd.

TETRA-CO-ORDINATION OF NICKEL (II)—III

VISIBLE AND ULTRA-VIOLET ABSORPTION SPECTRA OF $NiX_2 \cdot 2PR_3$ COMPLEXES

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Abstract—Visible and ultra-violet absorption spectra have been taken for complexes of the type $NiX_2 \cdot 2PR_3$ (X = NCS, Cl, Br; R = n-propyl, i-propyl, s-butyl, cyclohexyl). An assignment of the various transitions is suggested. Frequency shifts depending on alkyl substitution are shown to be due either to steric effects or to non-bonded group perturbations.

RECENT progress in ligand field theory has made possible calculation of the modification of the normally degenerate electronic energy-levels of transition metal ions when they become bound in a co-ordination compound.[1] A sufficiently rigorous identification of the characteristic absorption bands of these complexes has been achieved, by a judicious assignment to electronic transitions between the various levels originating from the total or partial disappearance of the degeneracy. These bands usually appear in the visible region and are of low intensity.

Owing to the large influence of the geometric arrangement of the ligands on the splitting of the levels, it is possible, under certain circumstances, to draw conclusions about the co-ordination by interpretation of the absorption spectra.[2]

MAKI[3] has calculated the splitting of singlet and triplet energy levels of Ni(II) ion in ligand fields of various symmetries and for a number of values of the field parameters (ligand-ion distance and dipole magnitude). She applied the results to the interpretation of the absorption bands arising from the central ion in different paramagnetic[4] compounds of nickel[5]; both in the solid state and in solution. One of the most important results was a semiquantitative explanation of the paramagnetism arising in solutions of various compounds which are diamagnetic in the solid state.

Similar calculations have been carried out by FURLANI[6] for Ni(II) complexes showing two magnetic forms in the solid state.

With these results in mind we thought it interesting to look at the spectroscopic behaviour of a series of complexes of Ni(II) with cyclohexylphosphine; of which we had already investigated the crystal structures and the dipole moments.[7] This series of compounds is structurally very similar to the triethylphosphine series[8] but there is an apparent "anomaly" in the bromide, which suggests a different intensity of the ligand field. It was our intention to see if the origin of this effect was a difference in the electronic situation of the phosphorus atom (due to alkyl substitution) or some other

[1] W. MOFFITT and C. J. BALLHAUSEN, *Ann. Rev. Phys. Chem.* **7**, 107 (1956).
[2] R. W. ASMUSSEN and O. BOSTRUP, *Acta Chem. Scand.* **11**, 1097 (1957).
[3] G. MAKI, *J. Chem. Phys.* **28**, 651 (1958).
[4] G. MAKI, *J. Chem. Phys.* **29**, 162 (1958).
[5] G. MAKI, *J. Chem. Phys.* **29**, 1129 (1958).
[6] C. FURLANI, *Gazz. Chim. Ital.* **88**, 279 (1958).
[7] A. TURCO, V. SCATTURIN and G. GIACOMETTI, *Nature, Lond.* **183**, 601 (1959).
[8] G. GIACOMETTI, V. SCATTURIN and A. TURCO, *Gazz. Chim. Ital.* **88**, 434 (1958).

Vol. 15 1960

cause, such as steric hindrance. The dipole moment measurements[7] seemed to support the latter view.

We have examined the ultra-violet and visible absorption spectra of some $NiX_2 \cdot 2PR_3$ compounds with X = SCN, Cl, Br, and R = cyclohexyl, i-propyl, n-propyl, and i-butyl.

EXPERIMENTAL

Complexes with n-propylphosphine were prepared according to JENSEN[9], those with cyclohexylphosphine as already described.[7] The complexes with s-alkylphosphines were obtained by adding the phosphine, prepared according to CULE DAVIES[10], to a solution of the nickel salts in 95 per cent ethanol. The properties of these previously unknown compounds, are as follows:

(1) $NiBr_2 \cdot 2P(i\text{-}Pr)_3$: red crystals (with green pleochroism); m.p. 151–154 °C; slightly soluble in methanol, ethanol, ethyl ether, fairly soluble in benzene; the solutions and the molten substance are olive-green.

(2) $NiCl_2 \cdot 2P(i\text{-}Pr)_3$: red crystals, solubility similar to the previous compound; solutions are red; m.p. 184–186 °C.

(3) $Ni(NCS)_2 \cdot 2P(i\text{-}Pr)_3$: orange-yellow crystals; solubility similar to the previous compound. Solutions are orange-yellow; m.p. 185–187 °C.

(4) $NiBr_2 \cdot 2P(s\text{-}Bu)_3$: very similar to (1); m.p. 91–93 °C.

(5) $NiCl_2 \cdot 2P(s\text{-}Bu)_3$: very similar to (2); m.p. 102–103 °C.

The absorption spectra were taken on a Beckman D.U. spectrophotometer. A number of solvents were tried. Spectra in benzene, cyclohexane and chlorobenzene were practically identical. Pyridine was also tried but on addition of benzene and partial evaporation, blue crystals separated from the solutions which gave, on analysis, the formula $NiX_2 \cdot 4Pyr$. These compounds were already known in the literature.[11] This observation shows that great caution is necessary in the study of spectra in solvents of high co-ordinating power. In carbon disulphide decomposition of the complexes with separation of phosphine, was observed, but no pure compound was isolated in this instance.

The concentrations used were of the order of 10^{-4} moles/l. in the regions of high extinction coefficient and about 2×10^{-3} moles/l. in the visible region. For the spectra of the solids the potassium bromide disk technique was used,[12] 1 mg of the complex being mixed with 300 mg of bromide.

RESULTS AND DISCUSSION

In Tables 1 and 2 the values of the frequency and molar extinction coefficients for the absorption maxima of the n-propyl and i-propyl phosphine complexes are summarized. The data for the compounds with R = cyclohexyl and s-butyl coincide within the experimental error with those of Table 1 and have not been reported.

Absorption spectra of $NiX_2 \cdot 2P(n\text{-}Pr)_3$ and $NiX_2 \cdot 2P(i\text{-}Pr)_3$ in benzene are shown in Figs. 1, 2 and 3. In Figs. 4, 5 and 6, solid and benzene solution spectra are compared for the series $NiX_2 \cdot 2PCy_3$ (visible region).

A qualitative examination of the spectra shows three absorption zones around the frequencies 35,000, 25,000 and 19,000 cm^{-1}.

The strong bands ($\log \varepsilon \approx 4$) of the first two zones must be attributed to ligand–metal charge transfer transitions.

The absorption around 35,000 cm^{-1} is very probably associated with the phosphine ligands since its frequency remains unaltered on changing the anion, It is also practically unchanged by alkyl substitution, indicating the limited importance of electronic

[9] K. A. JENSEN, *Z. Anorg. Chem.* **229**, 265 (1936).
[10] V. CULE DAVIES, *J. Chem. Soc.* 1043 (1933).
[11] M. A. PORAI-KOSHITS and A. S. ANTSISHKINA, *Dokl. Akad. Nauk SSSR* **92**, 333 (1953).
[12] M. M. STIMSON and M. J. O'DONNELL, *J. Amer. Chem. Soc.* **74**, 1085 (1952).

effects. The band is double with a maximum at 35,500–33,300 cm^{-1}. The only significant variation is an increase of the relative intensity of the shoulder on going from the halides to the thiocyanate.

The second absorption is almost certainly due to charge transfer from the anion to the metal, as is evident from the regular frequency shift observed in going from the bromide to the chloride to the thiocyanate. It is well known that these frequency

TABLE 1.—FREQUENCIES AND MOLAR EXTINCTION COEFFICIENTS OF ABSORPTION PEAKS OF $NiX_2 \cdot 2P(i\text{-}Pr)_3$ IN BENZENE

Band		X = NCS	Cl	Br
I	$\nu(cm^{-1})$	35,500–33,300	36,000–(33,300)	35,000–(33,300)
	log ε	4·2 4·3	3·5 (3·0)	3·9 (3·4)
II	$\nu(cm^{-1})$	—	—	(28,000)
	log ε	—	—	(<2·8)
III	$\nu(cm^{-1})$	26,600	25,500	23,400
	log ε	4·0	4·0	3·8
IV	$\nu(cm^{-1})$	(21,000)	19,150	17,300
	log ε	(<2·9)	<2·7	<2·7

TABLE 2.—FREQUENCIES AND MOLAR EXTINCTION COEFFICIENTS OF ABSORPTION PEAKS OF $NiX_2 \cdot 2P(n\text{-}Pr)_3$ IN BENZENE

Band		X = NCS	Cl	Br
I	$\nu(cm^{-1})$	35,500–33,300	36,000–(33,300)	36,000–(33,300)
	log ε	4·2 4·3	3·5 (3·0)	3·9 (3·4)
II	$\nu(cm^{-1})$	—	—	—
	log ε	—	—	—
III	$\nu(cm^{-1})$	27,200	26,900	25,150
	log ε	4·0	4·0	4·0
IV	$\nu(cm^{-1})$	(21,000)	20,400	18,650
	log ε	(<2·9)	<2·7	<2·6

shifts depend mainly on the anion ionisation potential (electron affinity of X), so that for higher electron affinities there is a shift to higher frequencies.[13] The frequency series NCS > Cl > Br is in agreement with this view. There are reasons, however, to believe that the position of the SCN ion in the spectrochemical series is dependent on whether it is co-ordinated through the sulphur or the nitrogen atom.[14] In the first case sulphur binding places SCN in the same position as Cl^- in the series,[15] while in the case of isothiocyanates the SCN band frequency is higher than for the chloride.

[13] H. L. SCHLÄFER, *Z. Phys. Chem. N.F.* **3**, 222 (1955).
[14] L. I. KATZIN, *J. Chem. Phys.* **20**, 1165 (1952).
[15] C. E. SCHÄFFER, *International Conference on Co-ordination Chemistry*, London, April, 1959, Abstr. No. 72.

Vol. 15 1960

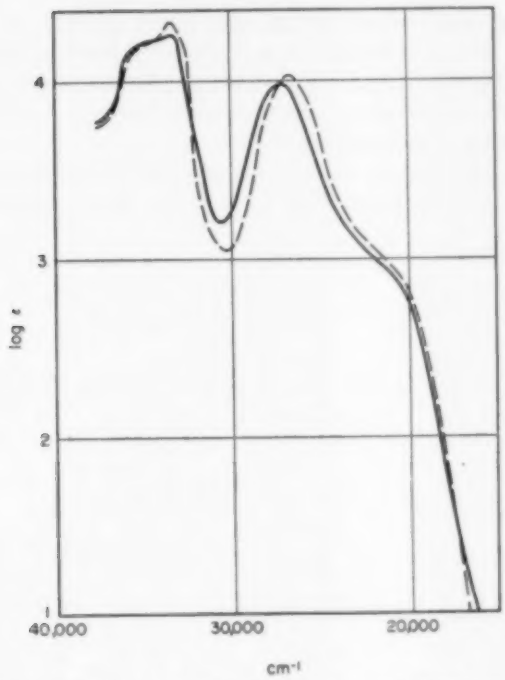

FIG. 1.—Absorption spectra of $Ni(NCS)_2 \cdot 2P(i\text{-}Pr)_3$ (– – – –) and $Ni(NCS)_2 \cdot 2P(n\text{-}Pr)_3$ (———) in benzene.

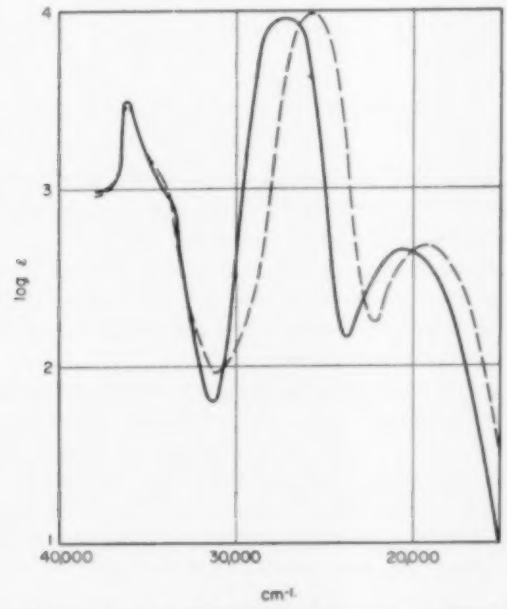

FIG. 2.—Absorption spectra of $NiCl_2 \cdot 2P(i\text{-}Pr)_3$ (– – – –) and $NiCl_2 \cdot 2P(n\text{-}Pr)_3$ (———) in benzene.

In the present case infra-red evidence has shown that the SCN ion is co-ordinated through the nitrogen atom, the complexes actually being isothiocyanato compounds. The position of the SCN in the above sequence is consequently the same as in the spectrochemical series, which was originally based solely upon $Cr(NCS)_6^{3-}$ in which the nitrogen is bonded to the chromium.[15,17]

The important feature of these bands is the significant red-shift on substituting the secondary alkyls by normal ones (see Figs. 1, 2 and 3). Similar behaviour is found in

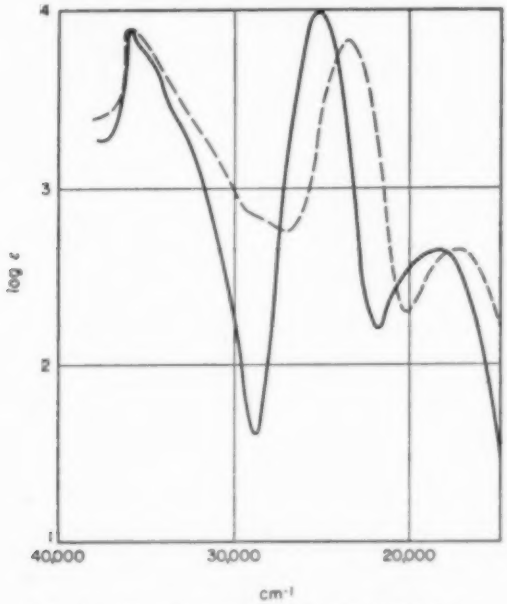

FIG. 3.—Absorption spectra of $NiBr_2 \cdot 2P(i\text{-}Pr)_3$ (– – – –) and $NiBr_2 \cdot 2P(n\text{-}Pr)_3$ (———) in benzene.

the third absorption region (in the visible), which is the most interesting from the point of view of ligand field theory. These absorptions correspond to *g-g* forbidden transitions among the electronic levels of the central ion.

Before discussing this behaviour in more detail it is better to examine the spectra obtained for the solids. These have been recorded only for the case of the sec-alkyl phosphines; where the anomalous behaviour of the change in colour in going from the solid state to solution can be observed.

The differences between solid and solution are limited to the visible region and are rather slight. They are practically limited to a stronger absorption in the high frequency region. It is especially marked in the halide compounds. These very slight spectral changes allow one to state quite definitely that there are no major structural changes (either electronic or molecular) upon solution. If there is an extra absorption band in the solids it is certainly due to a forbidden *g-g* transition, which gains intensity probably through coupling with some vibration of the right symmetry. It is possible

[16] C. PECILE, G. GIACOMETTI and A. TURCO, *Atti Acad. Naz. Lincei, Rend. Classe Sci. fis. mat. nat.* In press.
[17] R. TSUSHIDA, *Bull. Chem. Soc. Japan* **13**, 436 (1938).

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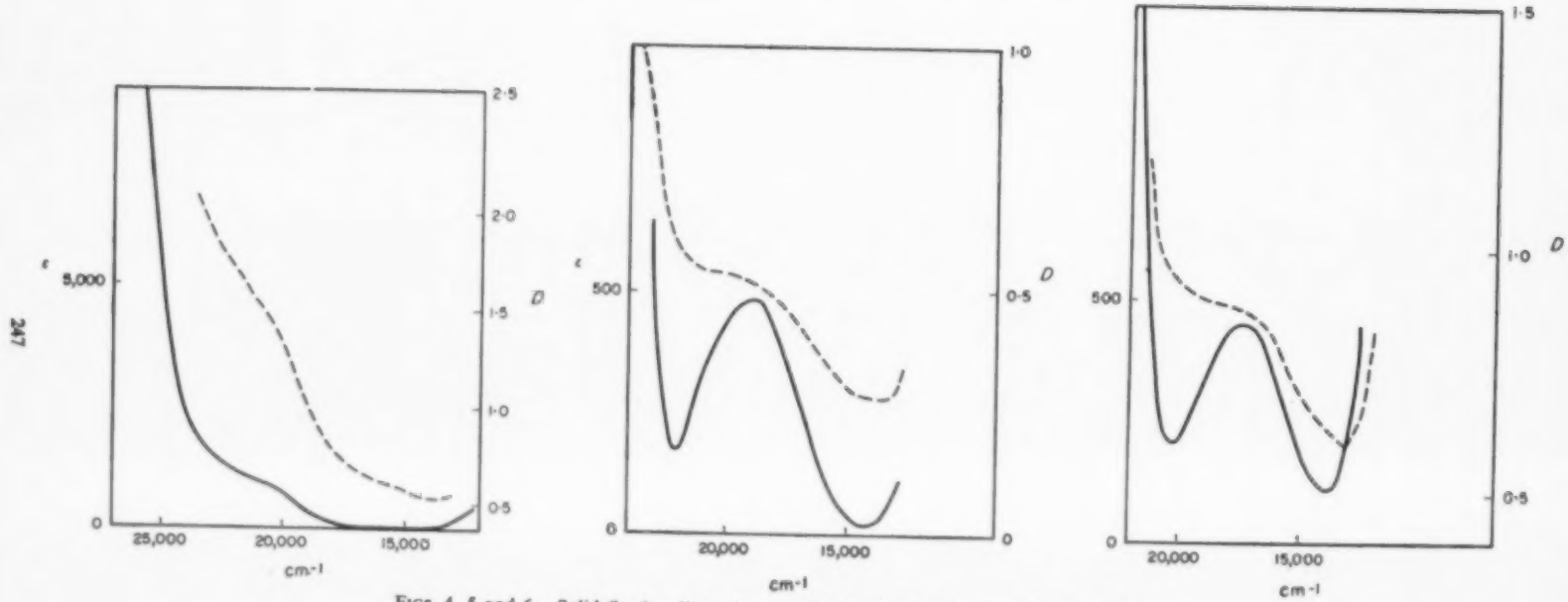

FIGS. 4, 5 and 6.—Solid (broken line; D = optical density) and benzene solution (full line; ε = molar extinction coefficient) spectra of complexes with cyclohexylphosphine.
Fig. 4: $Ni(NCS)_2 \cdot 2PCy_3$. Fig. 5: $NiCl_2 \cdot 2PCy_3$. Fig. 6: $NiBr_2 \cdot 2PCy_3$.

that the same band may also be found, with lower intensity, in solution. This absorption is obviously responsible for the strong pleochroism of the crystals of the halide complexes. It is not visible in the thiocyanate because it has shifted to the ultra-violet region. Measurements of the absorption of single crystals would be of great interest for these compounds.

Returning to the behaviour of the visible bands, we find that the shift towards lower frequencies in the series SCN, Cl, Br, is that normally expected from a progressive weakening of the ligand field and is in agreement with the position of the three anions in the spectrochemical series.

TABLE 3.—FREQUENCY DIFFERENCES FOR BANDS III AND IV BETWEEN i-Pr-PHOSPHINE AND n-Pr-PHOSPHINE COMPOUNDS

	$\Delta\nu$ (cm^{-1})		
Band	Br	Cl	NCS
III	1750	1400	600
IV	1350	1250	—

The substitution of normal by secondary alkyl groups in the phosphines also produces a weakening of the field. This cannot be explained by electronic effects; the electronic effect of the substitution would be to increase the electron density on the phosphorus atom and consequently to give rise to a more intense ligand field. Nor can the parallel shift in the anion-metal band be explained by electronic effects.

As a tentative explanation, we suggest that the most important effect might be steric hindrance, increasing from the phosphines with n-alkyls to those with s-alkyls. Steric hindrance between the ligands should affect the equilibrium anion-metal distance. In other words, increasing the steric hindrance due to the phosphine ligands, leads to co-ordination of the anions at slightly larger distances and produces weakening of the field.

This hypothesis also explains the shift of the metal-ion charge transfer bands. According to a very crude theory of these transitions,[13] the two states involved are:

$$X^- \ldots . (NiL_2)^{2+} \ldots . X^- \qquad X \ldots . (NiL_2)^{+} \ldots . X^-$$

If the electrostatic energy between oppositely charged ions is the most important term, then the energy difference between the two states decreases on increasing the Ni-X distance. The theory, although simple, is certainly suitable for qualitative predictions.

These conclusions are consistent with the fact that the shifts in the frequencies decrease in order of decreasing effective anionic size, i.e. Br > Cl > NCS (see Table 3)* However a Stuart model of the molecule fails to show the postulated steric effects unambiguously. It would appear that only a refined X-ray analysis, which would give the relevant bond distances, could provide evidence in support of this hypothesis.

The red-shift in band IV observed in passing from the n-propyl to the i-propyl complexes might however be accounted for in an alternative way, by considering

* If the NCS ion is co-ordinated through the nitrogen atom, the steric hindrance to co-ordination is smaller for NCS than for the chloride ion.

Vol. 15 1960

non-bonded group perturbations, as suggested by the work of T. M. DUNN and D. P. CRAIG (private communication). This shift could be interpreted in terms of the greater axial perturbation in these planar complexes by the methyl of the i-propyl group as compared with the n-propyl radical. The effect of the axial field is known to destabilize the ^1A_g ground state relative to the excited states.[3]

We have attempted to correlate the visible absorption data with the predictions that can be made on the basis of MAKI's calculations.[3] A complete energy level diagrams for the *trans*-planar (D_{2h}) field has been given for an effective ion-ligand distance of 1·5 Å and for a single value of the dipole moment (μ_1) of one pair of ligands the other (μ_2) being varied between zero and 2·5 μ_1. The choice of these ligand field parameters is largely subjective and there do not exist criteria for a sound selection. For this reason it is not worth while investigating other sets of parameters for the present case, but we feel that the diagram can be used for a qualitative comparison, probably being not very far from the truth. The interesting feature is that the range of values giving rise to a singlet ground state* is quite narrow and within this range the three transitions ^1A_g–$^1B_{3g}$, ^1A_g–$^1B_{1g}$ and ^1A_g–^1A_g may well be contained within a small frequency interval. This could explain the fact that the visible absorption region is probably a superposition of more than one band, as is evident from the discussion of the solid spectra and also from the observation that the bands in solution are quite broad and their extinction coefficient (~500) is larger than is usually found for *g-g* forbidden transitions (~100–200 at most). The 28,000 cm^{-1} band, which appears distinctly in the case of $NiBr_2$ complexes with cyclohexyl or i-propyl phosphines, could be assigned to the ^1A_g–$^1B_{2g}$ transition, which is predicted at high frequencies. In the other instances it is masked by the strong absorption at 33,000 cm^{-1}.

Acknowledgements—The authors wish to thank Dr. L. E. ORGEL for a revision of the manuscript and Dr. T. M. DUNN for helpful suggestions.

* The magnetic properties have only been determined for compounds with cyclohexylphosphine[7] and with n-alkylphosphines;[8] the spectral observations convince us, however, of the diamagnetism of the other complexes under discussion.

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CATALYSIS OF COMPLEX FORMATION REACTIONS*

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Abstract—The catalysed complex formation reactions can be classified into (1) co-ordination catalysis, (2) electron transfer catalysis, (3) induced complex formation, (4) heterogeneous catalysis. The general features of these types are outlined and the considerations are illustrated by characteristic examples.

THE catalytic phenomena of complex chemistry can be classified into two groups:

(1) catalysis of formation of complexes and
(2) catalysis by complex compounds.

Since these phenomena are extremely various, it is impossible to present a unified treatment. As far as we know this is the first attempt to systematize the catalysis of complex formation reactions. Dealing with the complex formation reactions it has to be considered that every formation reaction really is an exchange process. In the reactions which are termed commonly as formation reactions the displacement of solvent molecules bound in the co-ordination sphere occurs. The phenomena of catalysis of formation of complex compounds may be divided into three groups:

(i) co-ordination catalysis,
(ii) catalysis connected with redox reactions,
(iii) heterogeneous catalysis.

Vol.
15
1960

(i) *Co-ordination catalysis*

In the case of co-ordination catalysis the formation of the complex is preceded by a temporary formation of another complex.

(a) *Catalysis by ligand.* If the Me central ion reacts slowly with ligand A and rapidly with the B ligand—which forms a thermodynamically less stable complex—and the MeB complex reacts also rapidly with ligand A, then ligand B catalyses the formation of the MeA complex. Schematically:

$$\mathrm{Me} + \mathrm{A} \underset{}{\overset{k_1}{\rightleftharpoons}} \mathrm{MeA}$$

$$\mathrm{Me} + \mathrm{B} \overset{k_2}{\rightleftharpoons} \mathrm{MeB}$$

$$\mathrm{MeB} + \mathrm{A} \overset{k_3}{\rightleftharpoons} \mathrm{MeBA} \overset{k_3'}{\rightleftharpoons} \mathrm{MeA} + \mathrm{B}$$

$$k_2, k_3, k_3' > k_1$$

* Part of the paper presented at the International Conference on Co-ordination Chemistry, London, April, 1959.

A well known example of co-ordination catalysis is the catalytic effect of hydroxide ions on the formation of different complexes.[1,2] A specific catalytic phenomenon was observed by us in connection with the formation of Cr(III)–thiocyanate complex. The reaction was followed by the determination of formed neutral complex $[Cr(SCN)_3]$: aliquot parts of the reaction mixture were periodically shaken with isoamylalcohol, and the organic layer containing the neutral complex was examined spectrophotometrically.

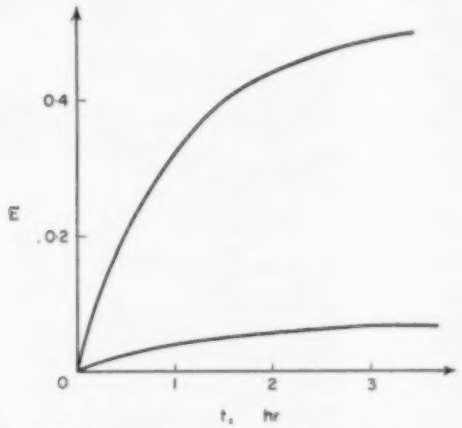

FIG. 1.—The change of absorbancy of aliquots at 420 mμ: $C_{Cr} = 0{\cdot}0277$ mole/l. $C_{SCN} = 0{\cdot}2710$ mole/l. Upper curve: pH adjusted to 4·2 by $NaHCO_3$ $I = 1{\cdot}03$. Lower curve: pH adjusted to 4·2 by $Ba(OH)_2$ $I = 1{\cdot}08$ $t = 25°C$.

Fig. 1 shows that the rate of reaction greatly varies depending on whether the pH of solutions was adjusted with barium hydroxide or sodium hydrogen carbonate. The pH of solutions being equal and the difference between the ionic strength negligible, the cause of the difference in reaction velocity is the different carbonate and *hydrogen*-carbonate content of solutions. Gasometric experiments showed that the amount of dissolved carbonic acid is *considerable*. So it is reasonable to suppose that the temporary formation of a Cr(III)–carbonate or Cr(III)–hydrogen-carbonate complex is responsible for the increased velocity. A similar catalytic effect of carbonate ion was not observed in formation of other Cr(III) complexes.

(b) *Catalysis by cation.** The acceleration effect of certain metal ions on the equation of different halogen complexes[3–6] also may be termed as co-ordination catalysis. In this case the accelerating effect can be ascribed to the temporary formation of a binuclear complex;[4,6] which may be formed either as the transition state or, in some cases have a more permanent existence.

$$MeX_{6-n}\,Hl + M \rightarrow X_{6-n}\,MeHlM \rightarrow MeX_{6-n}\,H_2O + MHl$$

The catalysis of aquation of monobromo–ethylenediaminetetraacetato–cobalt(III)

* This problem was not discussed in the lecture.

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[2] C. POSTMUS and E. L. KING, *J. Phys. Chem.* **59**, 1216 (1955).
[3] J. N. BRÖNSTED and R. LIVINGSTON, *J. Amer. Chem. Soc.* **49**, 435 (1927).
[4] P. J. ELVING and B. ZEMEL, *J. Amer. Chem. Soc.* **79**, 5855 (1957).
[5] W. C. E. HIGGINSON and M. P. HILL, *J. Chem. Soc.* 1620 (1959).
[6] M. T. BECK, Thesis, Szeged (1956).

complex by lead ion[5] may serve as an example of this type of reaction. Mention must be made that in this case we can speak about catalysis only with some reservation, the complex formed ($PbBr^+$) in this way being rather stable. Nevertheless it is beyond doubt that the reason of accelerating effect is the formation of a binuclear complex and not the combination of Pb^{2+} with dissociated bromide ions. Namely, according to our experiments, $Co(NH_3)_6(NO_3)_3$ has no effect on the rate of aquation, although it forms an "outer sphere" type complex with bromide ion the stability of which equals to that of the $PbBr^+$[7] ion. Naturally in this case there is no possibility that a binuclear complex is formed.

(ii) *Catalysis connected with redox reactions*

The following two examples of catalysis connected with redox reactions represent two different types, namely electron transfer catalysis and induced complex formation.

(a) If the following displacement reaction

$$MeA + B = MeB + A$$

where Me ion is in a higher oxidation state is accelerated by the Me ion in a lower oxidation state, the reason of catalysis is an electron transfer reaction.

An example of this type, the reaction of iron(III) xylenolorange complex with aminopolycarboxylic acids which is greatly catalysed by ferrous ion.[8] The reaction could be followed by spectrophotometric determination of concentration of iron(III)–xylenolorange complex. On the basis of our kinetic investigation of the reaction with 1,2 diaminocyclohexametetraacetic acid (Q) the mechanism of catalysis is as follows:

$$Fe(III)XO + Fe(II)Q = Fe(III)Q + Fe(II)XO$$

$$Fe(II)XO = Fe(II) + XO$$

Fe(II)Q is supplied by the following equilibrium

$$Fe(II) + Q = Fe(II)Q$$

which is shifted toward the dissociation at the given acidic medium. Considering the possible concentration of the Fe(II)Q complex, the ratio of the velocity constants of the catalysed and non-catalysed reactions is about 10^5.

(b) If the formation of a complex is accelerated by a simultaneous redox reaction the phenomenon may be termed as induced complex formation.

The oxidation of certain Co(II) amino acid complexes takes place in two steps.[9,10] First, an oxygen carrying Co(II) complex forms by a reversible oxygen uptake and then—in an irreversible reaction—the Co(III) complex forms. Both reactions are rather slow. We observed[11] that the Co(II) glycylglycine complex catalyses the autoxidation of ascorbic acid and the ascorbic acid accelerates the oxygenation of the Co(II)–glycylglycine complex, i.e. the formation of oxygen carrying complex. This latter phenomenon is shown in Fig. 2. where the change of absorbancy at about 520 mμ (filter S_{52}) is plotted as a function of time, in the presence and absence of ascorbic

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Vol. 15 1960

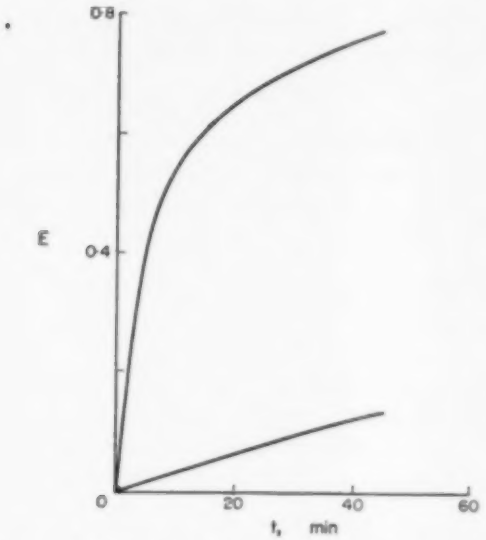

FIG. 2.—The change of absorbancy during the oxygenation of Co(II)–glycylglycine complex in presence (upper curve) and absence (lower curve) of ascorbic acid: $C_{Co} = 10^{-3}$ mole/l; $C_{asc.} = 10^{-2}$ mole/l; pH = 8; cuvette 3, 5 cm, filter S52.

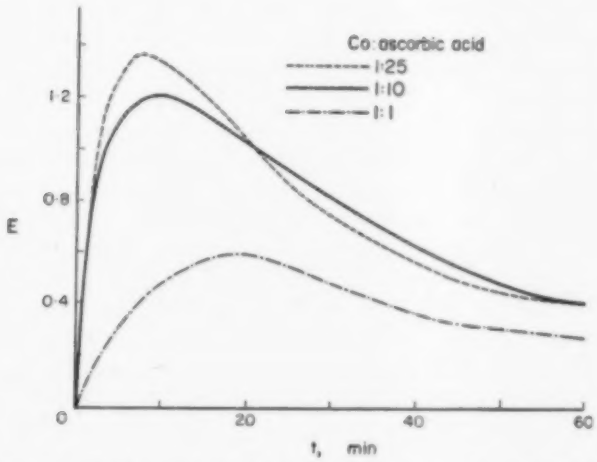

FIG. 3.—Effect of ascorbic acid on the formation of intermediate. $C_{Co} = 10^{-3}$ mole/l; pH = 7·5, cuvette 5 cm, wavelength 350 mμ. The molar absorbancy of oxygen carrying complex is 8000.

acid. In the visible region the absorbancy of oxygen carrying and the Co(III) complexes are the same, but in the near ultra-violet the absorbancy of the oxygen carrying complex is much higher than that of the Co(III) glycylglycine complex. So the change of concentration of the oxygen carrying complex with time can be observed by measuring the absorbancy at 350 mμ. Fig. 3 shows the effect of ascorbic acid on the formation of oxygen carrying Co(II) complex.

The induced complex formation and the catalysis of the autoxidation of ascorbic

acid can be explained by the step by step activation of molecular oxygen. In the first step the ascorbic acid forms a labile adduct with oxygen:

$$A + O_2 = AO_2$$

the collision of which with a Co(II)–glycylglycine complex results in the oxygen carrying complex reacting with a greater velocity than the reaction of oxygen with the Co(II)–glycylglycine complex:

$$Co(II)gg_2 + O_2 \xrightarrow{k_1} Co(II)gg_2O_2$$

$$Co(II)gg_2 + AO_2 \xrightarrow{k_2} Co(II)gg_2O_2 + A$$

$$k_2 > k_1$$

On the other hand the oxygen carrying complex oxidizes the ascorbic acid with greater velocity than the molecular oxygen does. Beside these reactions, an irreversible oxidation of the Co(II) complex takes place which results in the change of the concentration of the oxygen carrying complex in time according to a maximum curve.

(iii) *Heterogeneous catalysis*

The heterogeneous catalysis of displacement reactions of complexes is well known and frequently used for preparative purposes.[12] Nevertheless till now the mechanism of heterogeneous catalysis was not investigated. We studied the reactions of different Co(III) amines with ethylenediamintetraacetic acid catalysed by active carbon.[13] On the basis of the comparative study of different complexes the following reasonable mechanism is suggested*: The co-ordination sphere of the adsorbed complex ion—due to the adsorption—becomes less firm. The loosening of the co-ordination sphere results in an increased reactivity; the collision of the adsorbed complex ion with a ligand forming a thermodynamically more stable complex is more effective than a collision in the bulk of solution. Naturally, the loosening of the co-ordination sphere is inversely proportional to the symmetry of the complexes. The experimental findings are in accordance with this view: the hexammine–Co(III) reacts much slower than the aquopentammine–Co(III) or the chloropentammine–Co(III) complexes. The loosening of the co-ordination sphere on the effect of active carbon is exhibited in the acceleration of the reduction of complexes by ascorbic acid. The reduction of chloropentammine–Co(III) is very slow in acidic medium while in the presence of active charcoal the reduction takes place rapidly, but with a messurable rate, whilst at pH 5 the reduction is immediate. Under these circumstances the hexammine–Co(III) cannot be reduced.

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* This refers only to exchange reactions catalysed by active carbon.

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INTERACTION OF RUTHENIUM(III) CHLORIDE SOLUTION WITH 1,2,3-BENZOTRIAZOLE

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Abstract—This paper is part of a general study of the interaction of the platinum elements with 1,2,3-benzotriazole. Methods for the synthesis of several 1,2,3-benzotriazole co-ordination compounds of ruthenium with certain metals and with certain halides in varying yields and high purity are reported.

THIS paper arises from a continued study of the interaction of the platinum elements with 1,2,3-benzotriazole. The chemistry of the interaction of palladium, osmium and rhodium with 1,2,3-benzotriazole has been reported previously in some detail.[1–3]

The purposes of this study were to synthesize certain 1,2,3-benzotriazole co-ordination compounds of ruthenium and to investigate the stoicheiometry of the reactions.

EXPERIMENTAL

Materials. The stock ruthenium(III) chloride solution was prepared by dissolving a weighed amount of reagent grade ruthenium(III) chloride, obtained from A. D. Mackay, Inc., in a small amount of distilled water contained in a litre volumetric flask. Complete hydrolysis of the ruthenium (III) was prevented by the addition of 2 ml of concentrated hydrochloric acid and the resulting solution was then diluted to volume with distilled water. Gravimetric standardization of the ruthenium content of this solution was accomplished by using slight modifications of the Gilchrist-Wischers procedure.[4]

A stock solution of 1,2,3-benzotriazole contained in a 2 per cent acetic acid solution was prepared according to the procedure of WILSON and WILSON[5].

All other materials employed in this study were reagent grade chemicals. The precipitates were filtered using medium porosity sintered-glass crucibles, with the exception of the bromo and chloro compounds which required fine porosity sintered-glass crucibles.

Analysis. The ruthenium content in the compounds was determined, using an inert gas atmosphere, according to the Gilchrist–Wischers procedure.[4] Before analysis, the compounds were dried in an oven and cooled in a vacuum desiccator over magnesium perchlorate. This procedure was especially necessary before analysing the compounds that contained strontium, bromine or chlorine. These three compounds, when exposed to the atmosphere for long periods of time, gained approximately one molecule of water per formula weight of compound; however, the water content was easily removed at 100°C. Conventional methods of analysis were used for the quantitative determination of carbon, hydrogen, nitrogen, halogens and other metals contained in the ruthenium co-ordination compounds.

Preparation of $Na[RuO_2(C_6H_4N_3)_2]$, *a purple coloured compound.* Three 15 ml portions of ruthenium(III) chloride solution, containing $6{\cdot}12 \times 10^{-4}$ g per ml of ruthenium, were added to an Erlenmeyer flask containing 2 ml of absolute alcohol. Upon the addition of 10 ml of 2·5 per cent

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1,2,3-benzotriazole solution to each flask, the above solutions changed immediately from reddish-brown to a deep purple. To each of these solutions were added 10 ml of a saturated sodium hydroxide solution; then 3 ml of acetic acid were added to each solution after which deep purple coloured precipitates were produced. The precipitates were digested on a steam bath for 1 hr, then collected on sintered-glass crucibles, washed with several portions of hot water, and dried in an oven at 105°C to constant weight. Because of incomplete precipitation as indicated by the purple colour of the filtrate, gravimetric precision and accuracy were not studied. It was noted that alcohol was not necessary for precipitation to occur in the aforementioned basic medium; however, precipitation was more complete in the presence of alcohol. (Found: C, 36·50; H, 2·75; N, 21·24; Ru, 25·77; Na, 5·72. Calc. for $Na[RuO_2(C_6H_5N_3)_2]$: C, 36·55; H, 2·56; N, 21·31; Ru, 25·64; Na, 5·83%). The reaction described above seems to follow the path given below

$$Ru^{8+} + 2H_2O \xrightarrow{HCl} RuO_2^{-} + 4H^{+}$$

$$RuO_2^{-} + 2C_6H_5N_3 \longrightarrow [RuO_2(C_6H_5N_3)_2]^{-}$$

$$Na^{+} + [RuO_2(C_6H_5N_3)_2]^{-} \longrightarrow Na[RuO_2(C_6H_5N_3)_2].$$

Preparation of $Na[RuO_2(C_6H_5N_3)_2$, *a green coloured compound.* The purple precipitate was prepared as described in the previous preparation and then dissolved by the addition of an excess of acetic acid. The resulting acidic solution was digested for 1 hr on a steam bath and a beautiful green precipitate was produced. The precipitate was collected on a sintered-glass crucible and dried in an oven at 105°C to constant weight. Because of the green colouration remaining in the filtrate, gravimetric precision was not studied for this compound. (Found: C, 36·60; H, 2·44; N, 21·30; Ru, 25·70; Na, 5·78%).

Preparation of $Li[RuO_2(C_6H_5N_3)_2$. Several solutions of purple coloured complex were prepared as described in the first preparation and to each was added an excess of a saturated lithium chloride solution. A deep purple precipitate resulted. These precipitates were collected on sintered-glass crucibles, washed with several portions of hot distilled water, and dried for 1 hr in an oven to constant weight. Three 10 ml portions of the ruthenium(III) chloride stock solution gave the following weights of the precipitates: 22·6, 22·7 and 22·6 mg. Calc: 22·7 mg. Average yield: 99·6 per cent. (Found: C, 38·29; H, 2·96; N, 22·01; Ru, 26·80; Li, 1·91. Calc. for $Li[RuO_2(C_6H_5N_3)_2$: C, 38·10; H, 2·66; N, 22·22; Ru, 26·72; Li, 1·83%).

Preparation of $Mg[RuO_2(C_6H_5N_3)_2]_2$. The ruthenium–1,2,3-benzotriazole complex was prepared in the usual manner. Three portions of this solution were treated with an excess of a saturated solution of magnesium chloride which produced a beautiful purple precipitate. These precipitates were digested on a steam bath for 1·5 hr, cooled, filtered on sintered-glass crucibles, washed with several portions of hot distilled water, and dried to constant weight for 1 hr in an oven. Because of the slight colour remaining in the solution, precision and accuracy were not studied. (Found: C, 37·33; H, 2·84; N, 22·51; Ru, 26·56; Mg, 3·18. Calc. for $Mg[RuO_2(C_6H_5N_3)_2$: C, 37·58; H, 2·63%).

Preparation of $Sr[RuO_2(C_6H_5N_3)_2]$. Three 10 ml portions of stock ruthenium(III) chloride solution were treated to produce the ruthenium–1,2,3-benzotriazole complex as described previously. An excess of strontium nitrate solution was added to these solutions producing a wine-red coloured precipitate. These precipitates were digested on a steam bath for 1 hr, filtered, washed and dried to constant weight for 1 hr in an oven at 105°C. Gravimetric precision and accuracy were not studied because of incomplete precipitation. (Found: C, 34·70; H, 2·45; N, 20·05; Ru, 24·35; Sr,10·52. Calc. for $Sr[RuO_2(C_6H_5N_3)_2]_2$: C, 34·72; H, 2·43; N, 20·24; Ru, 24·35; Sr, 10·55%).

Preparation of $K[RuO_2(C_6H_5N_3)_2]$. Three 10 ml aliquots of stock ruthenium(III) chloride solution were made to undergo the reaction which produces the purple ruthenium–1,2,3-benzotriazole complex. To this complex were added an excess of a saturated potassium hydroxide solution and 3 ml of acetic acid to effect precipitation. A beautiful purple precipitate resulted which was digested for 1·5 hr on a steam bath. The precipitates were cooled, filtered and dried to constant weight in the usual manner. The weight of the precipitates were as follows: 24·5, 24·7 and 24·7 mg. Calc: 24·7 mg. Average yield: 99·6 per cent. (Found: C, 35·01; H, 2·59; N, 20·74; Ru, 24·70; K, 9·47. Calc. for $K[RuO_2(C_6H_5N_3)_2]$: C, 35·11; H, 2·46; N, 20·48; Ru, 24·63; K, 9·53%).

Preparation of $Pb[RuO_2(C_6H_5N_3)_2]_2$. Three 10 ml aliquots of stock ruthenium(III) chloride solution were treated to produce the purple ruthenium–1,2,3-benzotriazole complex. An excess of saturated lead nitrate solution was added to each portion producing a purple precipitate. The

Vol. 15 1960

precipitates were digested on a steam bath for one hour, allowed to cool, filtered, and dried to constant weight. The weights of the precipitates were as follows: 56·9, 57·3 and 57·2 mg. Calc.: 57·2 mg. Average yield: 99·8%. (Found: C, 30·02; H, 2·34; N, 18·10; Ru, 21·29; Pb, 21·70. Calc. for $Pb[RuO_2(C_6H_5N_3)_2]_2$: C, 30·35; H, 2·12; N, 17·70; Ru, 21·29; Pb, 21·81%).

Preparation of $[RuOI(C_6H_5N_3)_2]$. Three 10 ml portions of the stock ruthenium(III) chloride solution were made to undergo the reacting which produces the sodium ruthenium–1,2,3-benzotriazole complex. To the resulting solutions were added excess amounts of hydroiodic acid and of sodium iodide. When the hydroiodic acid was introduced into these solutions, a beautiful dark green precipitate was formed. The sodium iodide was necessary for complete precipitation to be effected. After setting for 2 hr, the precipitates were well formed. The precipitates were filtered, washed with several portions of hot water, and dried to constant weight in an oven at 110°C. The weights of the precipitates were as follows: 29·1, 29·0 and 29·0 mg. Calc.: 29·0 mg. Average yield: 100 per cent. (Found: C, 29·44; H, 1·89; N, 17·83; Ru, 21·01; I, 26·56. Calc. for $[RuOI(C_6H_5N_3)_2]$: C, 29·89; H, 2·09; N, 17·43; Ru, 20·96; I, 26·32%). The reaction probably proceeds as

$$[RuO_2(C_6H_5N_3)_2]^- + 2HI \xrightarrow[HI]{NaI} [RuOI(C_6H_5N_3)_2] + I^- + H_2O$$

Preparation of $[RuOBr(C_6H_5N_3)_2]$. Three 1 ml portions of the stock ruthenium (III) chloride solution were treated in the usual manner to produce the sodium ruthenium–1,2,3-benzotriazole complex. To these solutions were added an excess of concentrated hydrobromic acid and an excess of sodium bromide. A fine purple precipitate resulted and the mixtures were allowed to stand for 2 hr. The precipitates were collected on crucibles, and dried to constant weight at 105°C. The weights of the precipitates were: 27·3, 27·0 and 27·0 mg. Calc.: 27·2 mg. Average yield: 99·6 per cent. (Found: C, 32·94; H, 2·37; N, 19·40; Ru, 23·24; Br, 18·28. Calc. for $[RuOBr(C_6H_5N_3)_2]$: C, 33·11; H, 2·32; N, 19·31; Ru, 23·23; Br, 18·36%).

Preparation of $[RuOCl(C_6H_5N_3)_2]$. Three aliquots of the ruthenium–1,2,3-benzotriazole complex were treated with an excess of concentrated hydrochloric acid and an excess of sodium chloride. There was no apparent reaction at room temperature; however, upon heating the mixtures, a purple precipitate was formed. The precipitates were digested for 2 hr on a steam bath, cooled, collected and dried in an oven at 105°C to constant weight. The weights of the precipitates were as follows: 24·5, 24·7 and 24·7 mg. Calc.: 24·6 mg. Average yield: 100 per cent. (Found: C, 36·93; H, 2·61; N, 21·45; Ru, 25·85; Cl, 8·91. Calc. for $[RuOCl(C_6H_5N_3)_2]$: C, 36·88; H, 2·58; N, 21·51; Ru, 25·87; Cl, 9·07%).

DISCUSSION

In this investigation, the chemistry of the interaction of ruthenium with 1,2,3-benzotriazole has been studied. Certain of the reactions appear to be simple metatheses in which Na^+ is replaced by some other cation or in which O^{2-} is replaced by a halogen ion (X^-). Weight relationships and elemental analysis indicate that an alcoholic aqueous solution of ruthenium(III) chloride reacts with 1,2,3-benzotriazole to form a complex ion of composition $[RuO_2(C_6H_5N_3)_2]^-$. The interaction of ruthenium with 1,2,3-benzotriazole suggests that an ionic species of $HRuO_2$ or RuOOH probably exists in solution and in either case ruthenium would be expected to exhibit an oxidation state of +3.

When $Na[RuO_2(C_6H_5N_3)_2]$ was precipitated from a basic solution, a purple precipitate was obtained. A green precipitate was obtained from a acid solution. Elemental analysis of both compounds corresponded to the general formula, $Na[RuO_2(C_6H_5N_3)_2]$. It was observed that the green sodium–ruthenium 1,2,3-benzotriazole co-ordination compound decomposes slowly when exposed to the atmosphere and diffuse light. Both the purple and green compounds, which are probably isomers, were slightly soluble in neutral and basic media, but insoluble in acidic media. The halogen compounds formed in the interaction of ruthenium with 1,2,3-benzotriazole were insoluble in neutral and acidic media, but they were very soluble in basic media. Also,

the co-ordination compounds of lithium, potassium, magnesium and lead were either insoluble or very slightly soluble in neutral and acidic media, but they were very soluble in basic media.

Further investigation on these compounds include plans for the application of magnetic susceptibility, thermogravimetric analysis and X-ray studies for the purpose of elucidating the structures of these interesting compounds.

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Vol.
15
1960

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OBSERVATIONS ON THE RARE EARTHS—LXXII*

THE PREPARATION AND CHARACTERIZATION OF ANHYDROUS AND N,N-DIMETHYLFORMAMIDE-SOLVATED ACETATES

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Abstract—Rare-earth metal and yttrium acetates have been effectively dehydrated by treatment with N,N-dimethylformamide and benzene, followed by azeotropic distillation. Ansolvous acetates, $Ln(C_2H_3O_2)_3$, have been obtained where Ln = Y, La, Dy, Ho, Er, and Yb; but where Ln = Ce(III), Pr, Nd, Sm, Eu, or Gd, monosolvated acetates, $Ln(C_2H_3O_2)_3 \cdot DMF$, have resulted. The latter compounds are readily converted to the ansolvous materials by heating *in vacuo* at 210°C. Ansolvous and dimethylformamide-solvated acetates have been characterized by means of analysis, X-ray diffraction, and infra-red measurements.

REPORTED metnods for the synthesis of anhydrous rare-earth metal acetates include

(1) the reaction of the hydrated nitrates with acetic anhydride,[1–3]
(2) the reaction of the oxides with fused ammonium acetate,[4] and
(3) the reaction of the oxides with acetic anhydride.[5]

The first procedure apparently yields oxo-acetates rather than acetates,[5] and the second procedure yields impure products.[4] The third procedure has given analytically pure anhydrous acetates with at least neodymium and samarium.[5]

Very little information exists on solvated acetates other than hydrates. Various basic species containing acetic acid of solvation have been recovered from acetic acid systems.[5] Disolvates of lanthanum and cerium(III) acetates have been reported to result from crystallization from anhydrous ethylene glycol,[6] but these may be solvates of basic salts since the acetate samples were prepared by the first procedure outlined above.

A new and somewhat different approach to the preparation of anhydrous rare-earth metal salts involves treating a hydrated salt with N,N-dimethylformamide(DMF), adding benzene, and distilling azeotropically to remove water.[7,8] Application of this procedure to the acetate systems has yielded anhydrous acetates with La, Dy, Ho, Er, Yb and Y and monosolvated acetates of the type $Ln(C_2H_3O_2)_3 \cdot DMF$ with Ce(III), Pr, Nd, Sm, Eu, and Gd. Complete desolvation of compounds of the latter type has been effected at ca. 210°C.

* For Part LXXI, see T. MOELLER and V. GALASYN, *J. Inorg. Nucl. Chem.* **12**, 259 (1959).

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TABLE 1.—PROPERTIES OF PRODUCTS FROM AZEOTROPIC DISTILLATION

Symbol	Analytical data				Melting point (°C)
	Found		Calculated		
	%	Atom ratio	%	Atom ratio	
$La(C_2H_3O_2)_3$					
La	43·40	1·00	43·95	1	
C	23·20	6·18	22·80	6	
H	2·98	9·42	2·87	9	
$Ce(C_2H_3O_2)_3 \cdot DMF$					
Ce	35·71	1·00	35·88	1	148–155
C	27·78	9·08	27·77	9	
H	4·10	15·96	4·11	16	
N	3·54	0·99	3·59	1	
$Pr(C_2H_3O_2)_3 \cdot DMF$					
Pr	35·90	1·00	36·01	1	151–155
C	27·61	9·02	27·63	9	
H	3·94	15·32	4·10	16	
N	3·63	1·01	3·58	1	
$Nd(C_2H_3O_2)_3 \cdot DMF$					
Nd	36·35	1·00	36·58	1	151–155
C	27·78	9·18	27·40	9	
H	4·11	16·20	4·07	16	
N	3·47	0·98	3·55	1	
$Sm(C_2H_3O_2)_3 \cdot DMF$					
Sm	37·22	1·00	37·55	1	137–140
C	27·30	9·19	26·98	9	
H	4·07	16·32	4·02	16	
N	3·60	1·04	3·50	1	
$Eu(C_2H_3O_2)_3 \cdot DMF$					
Eu	37·80	1·00	37·80	1	137–140
C	26·82	8·98	26·88	9	
H	3·94	15·72	3·99	16	
N	3·47	0·996	3·48	1	
$Gd(C_2H_3O_2)_3 \cdot DMF$					
Gd	38·42	1·00	38·60	1	
C	26·59	9·09	26·53	9	
H	3·88	15·80	3·94	16	
N	3·45	1·01	3·44	1	
$Dy(C_2H_3O_2)_3$					
Dy	44·30	1·00	47·84	1	
C	20·40	5·92	21·22	6	
H	2·96	10·77	2·67	9	

Vol. 15 1960

TABLE 1.—*continued*

Symbol	Analytical data				Melting point (°C)
	Found		Calculated		
	%	Atom ratio	%	Atom ratio	
$Ho(C_2H_3O_2)_3$					
Ho	44·10	1·00	48·20	1	
C	20·61	6·42	21·07	6	
H	3·04	11·30	2·65	9	
$Er(C_2H_3O_2)_3$					
Er	48·53	1·00	48·58	1	
C	20·85	5·99	20·89	6	
H	2·74	9·37	2·63	9	
$Yb(C_2H_3O_2)_3$					
Yb	49·53	1·00	49·40	1	
C	20·57	5·99	20·58	6	
H	2·57	8·91	2·59	9	
$Y(C_2H_3O_2)_3$					
Y	33·32	1·00	33·41	1	
C	27·19	6·04	27·08	6	
H	3·40	9·01	3·41	9	

EXPERIMENTAL

Materials, apparatus and techniques. Commercially available N,N-dimethylformamide was dried by the method of THOMAS and ROCHOW[9]. Reagent quality benzene was dried over freshly-cut sodium and then distilled. Rare-earth metal oxides of 99+ per cent purity were obtained from the Lindsay Chemical Division of the American Potash and Chemical Company. Reagent quality cerium(III) sulphate was obtained from the G. F. Smith Chemical Company.

Infra-red spectra were obtained with a Perkin–Elmer Model 21 Double-Beam Recording Spectrophotometer, using suspensions in Nujol between rock salt plates. X-ray diffraction data were obtained with a General Electric XRD-3 Diffraction Unit, using copper K_α radiation.

All compounds were analysed for rare-earth metal content by igniting at 900°C and weighing the resulting oxides. Carbon, hydrogen and nitrogen were determined by the usual micro-analytical methods.

Preparation of hydrated acetates. These were prepared in general by treating the respective oxides or hydroxides with glacial acetic acid and evaporating to crystallization.[10] Oxidation was avoided with cerium by converting cerium(III) sulphate to the carbonate and then adding glacial acetic acid. Praseodymium oxide, Pr_6O_{11}, was first reduced with hydrazine hydrate before the acetic acid treatment.[11] None of the hydrated acetates was analysed.

Dehydration of hydrated acetates. To 10 g of the hydrated rare-earth metal acetate in a 500 ml round-bottomed flask, 100 ml of dry N,N-dimethylformamide was added. The flask was shaken thoroughly to dissolve as much of the acetate as possible.* Then 150 ml of dry benzene was added, and the benzene–water azeotrope was removed by distillation, using a 3 ft glass column packed

* The acetates of Eu, Gd, Dy, Ho and Y dissolved readily; those of Pr, Nd and Sm dissolved completely only during distillation of the azeotrope; those of La, Ce(III), Er and Yb were slightly soluble or insoluble throughout.

[9] A. B. THOMAS and E. G. ROCHOW *J. Amer. Chem. Soc.* 79, 1843 (1957).
[10] GMELIN–KRAUT'S, *Handbuch der anorganischen Chemie* Auflage 7, Band VI, Abteilung 2, p. 47. Carl Winter's Universitätsbuchhandlung, Heidelberg (1932).
[11] R. GHER, Bachelor's dissertation, University of Illinois (1948).

with ¼ in. i.d. glass helices and wrapped with asbestos. The remaining benzene and a small quantity of dimethylformamide were then removed by continued distillation. Clear solutions remained except with yttrium, lanthanum, cerium(III), erbium and ytterbium.

Characteristically coloured crystals were deposited, except with dysprosium and holmium, when these solutions were cooled to room temperature. The crystals were washed with anhydrous ether and redissolved by refluxing with 40–60 ml portions of anhydrous N,N-dimethylformamide. Crystals deposited on subsequent cooling were washed with dry ether and dried *in vacuo* over anhydrous calcium chloride and phosphorus(V) oxide. The dysprosium and holmium compounds were obtained by evaporating to solids under reduced pressure, washing the residues repeatedly with dry ether, removing the ether *in vacuo*, and heating at 100°C for 1½ hr.

TABLE 2.—ANALYTICAL DATA FOR PRODUCTS OF DESOLVATION

Symbol	Found		Calculated	
	%	Atom ratio	%	Atom ratio
$Ce(C_2H_3O_2)_3$				
Ce	43·90	1·00	44·15	1
C	22·40	5·68	22·71	6
H	2·96	9·37	2·86	9
$Pr(C_2H_3O_2)_3$				
Pr	44·16	1·00	44·30	1
C	22·23	5·91	22·66	6
H	3·00	9·50	2·85	9
$Nd(C_2H_3O_2)_3$				
Nd	44·82	1·00	44·91	1
C	22·45	6·02	22·42	6
H	3·02	9·65	2·86	9
$Sm(C_2H_3O_2)_3$				
Sm	46·10	1·00	45·91	1
C	21·66	5·89	22·00	6
H	2·88	9·32	2·77	9
$Eu(C_2H_3O_2)_3$				
Eu	46·27	1·00	46·20	1
C	21·70	5·80	21·90	6
H	2·98	9·71	2·76	9
$Gd(C_2H_3O_2)_3$				
Gd	47·14	1·00	47·05	1
C	21·40	5·95	21·56	6
H	2·80	9·26	2·71	9

Lanthanum acetate was recovered directly from the reaction mixture as a result of its very low solubility. With cerium(III), yttrium, erbium and ytterbium, partial solubility permitted removal of the bulk of the product by direct filtration of the reaction mixture and the recovery of the remainder by evaporation of the mother liquor. Each compound was washed with anhydrous ether and dried as described above. Analyses of insoluble and crystallized materials were identical for each compound in the particular class.

Dehydration of solvated acetates. Anhydrous acetates were obtained from the monosolvates, $Ln(C_2H_3O_2)_3 \cdot DMF$, by heating in an Abderhalden drying apparatus at 210°C.

Vol. 15 1960

RESULTS AND DISCUSSION

Analytical data summarized in Table 1 indicate compositions very close to $Ln(C_2H_3O_2)_3 \cdot DMF$, where Ln = Ce(III), Pr, Nd, Sm, Eu and Gd, and $Ln(C_2H_3O_2)_3$, where Ln = La, Y, Er and Yb, for the products obtained by the dimethylformamide-benzene dehydration process. The dysprosium and holmium compounds approach ansolvous acetates, but are apparently basic salts. Analytical data summarized in Table 2 indicate complete conversion of the monosolvates into anhydrous acetates on heating. The yield in each instance is high but difficult to judge exactly because of the uncertain composition of the initial hydrated acetate.

TABLE 3.—INFRA-RED FREQUENCIES (cm^{-1}) FOR VARIOUS ACETATES

Compound										Assignment
A*	B	C	D	E	F	G	H	I	J	
	1658	1660			1660	1665				$—CONH_2$
				1590						
1550	1565	1555	1565	1550	1555	1560			1545	C=O stretching (unsym.)
1440	1460		1445		1458		1460	1462	1450	C=O stretching (sym.)
		1425			1420	1430				CH_3 deformation
	1375						1375	1377	1377	C—C stretching and
1345		1338	1340	1343	1340					C—O rocking
				1330						
	1255	1255			1255	1255				$—CONH_2$ (?)
	1118	1120			1120	1120				$—CONH_2$ (?)
								1075	1076	
	1055	1055	1050	1057	1055				1050	CH_3 rocking
1020	1015	1015	1020	1025	1015		1010		1015	
935	945	948	938	945	948		940		938	C—C stretching
		860								
							718	715	715	
660	660	668	662	670	665		665		668	COO deformation

* A—$Ce(C_2H_3O_2)_3$
B—$Ce(C_2H_3O_2)_3 \cdot DMF$
C—$Pr(C_2H_3O_2)_3 \cdot DMF$
D—$Nd(C_2H_3O_2)_3$
E—$Nd(C_2H_3O_2)_3$ (Ref. 14)
F—$Nd(C_2H_3O_2)_3 \cdot DMF$
G—$Sm(C_2H_3O_2)_3 \cdot DMF$
H—$Dy(C_2H_3O_2)_3$
I—$Ho(C_2H_3O_2)_3$
J—$Y(C_2H_3O_2)_3$

Both $Ln(C_2H_3O_2)_3 \cdot DMF$—and $Ln(C_2H_3O_2)_3$—type compounds dissolve readily in water but are only slightly soluble or insoluble in cold anhydrous N,N-dimethylformamide, ethanol or acetic acid. Large crystals of the monosolvates can be grown by slowly cooling solutions in dimethylformamide. All the compounds are insoluble in dry ether. Except for the cerium(III) compound, the monosolvates melt without loss of N,N-dimethylformamide, but at 200°C or above, desolvation is complete. The ansolvous acetates are somewhat hygroscopic; the monosolvates are either non-hygroscopic or only slightly so.

Evaluation of *d*-spacings from X-ray diffraction data for powder samples[12] shows the hydrated, dimethylformamide-solvated, and ansolvous acetates to be entirely different from each other. As may be expected, there are similarities among

[12] For a complete tabulation of these data, see T. MOELLER, G. W. CULLEN, V. D. GALASYN, D. S. SMITH, G. C. GIFFIN and J. XAVIER, Final report, AF 18(600)-1535, University of Illinois (1959).

the various compounds of each of these three classes that suggest structural similarities. The patterns were all well-defined. Unlike the dimethylformamide-solvated iodides,[13] the analogously solvated acetates underwent no detectable decomposition on exposure to X-rays. This stability, coupled with the ease of obtaining both clean-cut X-ray diffraction patterns and large crystals of the compounds, suggests the feasibility of a detailed crystal structure evaluation of compounds of the type $Ln(C_2H_3O_2)_3 \cdot DMF$.

Infra-red data summarized in Table 3 indicate retention of the carbonyl amide band, which appears at about 1665 cm^{-1} for pure N,N-dimethylformamide, by the solvates $Ln(C_2H_3O_2)_3 \cdot DMF$ without material displacement. It appears unlikely, therefore, that in these crystalline compounds there is strong interaction between the rare-earth metal ion and the carbonyl oxygen of the dimethylformamide. This, plus the observed ease of loss of dimethylformamide and the fact that only certain of the acetates crystallize with dimethylformamide, suggests that the solvating agent is occupying a lattice position that does not require a strong bond to the cation. The two strong bands at 1430 cm^{-1} and 1560 cm^{-1} due to the carboxyl group in the acetate ion are characteristic of both solvated and ansolvous compounds. Data for ansolvous neodymium acetate are in substantial agreement with those previously reported.[5,14]

Acknowledgement—The authors are indebted to the Air Force Office of Scientific Research for the financial support that rendered this investigation possible. The work was done under Contract AF 18(600)-1535.

[13] T. MOELLER and V. GALASYN, *J. Inorg. Nucl. Chem.* **12**, 259 (1959).
[14] J. A. SEATON, Doctoral dissertation, University of Illinois (1958).

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol 15, pp. 265 to 271. Pergamon Press Ltd.

PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTH ELEMENTS—III

CERIUM(III) TRIPOLYPHOSPHATES

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Abstract—The reaction between cerium(III) chloride and sodium triphosphate solutions has been discussed. Evidences have been obtained that cerium(III) and triphosphate ions form two insoluble compounds in which the ratios Ce^{3+}: $P_3O_{10}^{5-}$ are respectively 5 : 3 and 1 : 1. With excess triphosphate ions a stable solution is obtained.

The characteristic absorption spectrum of cerium(III) chloride solutions is changed upon addition of excess sodium triphosphate as a result of the formation of relatively stable complex species.

A new maximum between 300–304 mμ is observed. By the method of continuous variations, the complex is formed in the ratio Ce^{3+} : $P_3O_{10}^{5-}$ = 1 : 2, in the pH range of 3·0–9·5.

THE complexing action of sodium triphosphate has been recognized for many years.[1] In a previous communication,[2] the reactions of yttrium and neodymium ions with sodium triphosphate were described and their possible utility in effecting separations of the rare earth elements from each other and of the rare earth elements from accompanying elemental species was pointed out.

The behaviour of cerium(III) chloride solutions with sodium triphosphate is almost the same as that observed with yttrium and neodymium ions. The precipitate formed by the addition of sodium triphosphate to cerium(III) chloride solutions is easily dissolved by an excess of triphosphate ions, giving stable solutions.

Cerium(III) bands, unlike those of the ions in the region praeseodymium(III)–thulium(III), are due to changes in configuration involving the valence shell and may thus be expected to change on addition of a complexing agent. Cerium(III) ion shows strong absorption bands in the ultra-violet region.[3,4] and it is of interest to observe now if this spectrum changes upon addition of triphosphate ion. LOUGHRAN[5] observed that on addition of increasing amounts of sodium triphosphate to copper nitrate solutions the extinction of the same band increases approaching a maximum value in solutions containing a large excess of triphosphate. HOJMAN[6] investigated the effect of pH and that of the concentration of citric acid upon the absorption spectra of cerium(III) chloride solutions. The compositions of the cerous citrate complexes at different pH were determined by the method of continuous variations.

In our experiments, it was early observed that the original spectrum of cerium(III)

[1] L. FRANKENTHAL, J. S. ROBERTS and C. NEUBERG, *Exp. Med. Surgery* **1**, 395 (1943).
[2] E. GIESBRECHT and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* **6**, 308 (1958).
[3] T. MOELLER and J. C. BRANTLEY, *Analyt. Chem.* **22**, 433 (1950).
[4] D. C. STEWART and D. KATO, *Analyt. Chem.* **30**, 164 (1958).
[5] E. D. LOUGHRAN, Thesis, The Ohio University (1955).
[6] I. M. HOJMAN, *Bull. Inst. Nucl. Sci.* "*Boris Kidrich*" **84**, 88 (1955).

chloride solutions was strongly modified. A new absorption band was observed, and the original maxima were shifted to longer wavelengths. The dissolution of the cerium(III) triphosphate which is first precipitated is easily obtained by adding a sufficient excess of triphosphate to make the ratio $Ce^{3+} : P_3O_{10}^{5-}$ at least 1 : 1·5. The stability of these solutions increases with the increasing ratio of triphosphate ion to cerium(III) ion.

The influence of pH is considerable and should be considered together with the ratio between the ions. When the ratio of triphosphate ion to cerium(III) ion is small, the influence of pH is pronounced and the solutions which are obtained are stable only over small pH ranges (See Experimental section). When the ratio increases the influence of pH is smaller. The solutions are then stable over larger pH ranges, and the absorption spectra remain unchanged for long periods.

This can be explained in terms of the dissociation of the triphosphoric acid.[7] The ionic species $P_3O_{10}^{5-}$ is predominant at high pH and the possibility of formation of a complex between cerium(III) and triphosphate ions increases, specially by increasing the ratio of triphosphate ion to cerium(III) ion. When the pH drops one has to consider the presence of other ions of the type $H_nP_3O_{10}^{5-n}$ which exert their own influence by forming other complexes with cerium(III) ions, as suggested by the spectrophotometric curves obtained in the low pH range. Complexes of this type were recently described in the literature.[7,8]

Potentiometric titrations have given different results from those obtained by the previous method. The formation of an insoluble compound with the ratio $Ce^{3+} : P_3O_{10}^{5-} = 1 : 1$ was observed when cerium(III) chloride solutions were titrated with sodium triphosphate solutions. The back titrations did not show the formation of that and any other compound between cerium(III) and triphosphate ions.

Conductometric titrations of cerium(III) chloride with sodium triphosphate solutions showed the formation of two insoluble compounds—normal cerium(III) triphosphate, $Ce_5(P_3O_{10})_3$ and another one in which the ratio $Ce^{3+} : P_3O_{10}^{5-}$ is 1 : 1. Back titration did not indicate the formation of any compound. A soluble complex between cerium(III) and triphosphate ion was not detectable even in very dilute solutions.

Attempts to isolate the insoluble compounds in a pure form were not successful. The results obtained for cerium and phosphorus did not correspond either to normal cerium(III) triphosphate or to a compound in which the ratio $Ce^{3+} : P_3O_{10}^{5-}$ is 1 : 1. In all cases, the data were in accordance with a mixture of the two substances.

EXPERIMENTAL

The sodium triphosphate, $Na_5P_3O_{10}·6H_2O$, was prepared from anhydrous sodium triphosphate, supplied by the Victor Chemical Trading Corporation. The anhydrous salt was purified according to a procedure described by WATTERS *et al.*[9] and its purity was checked by a phosphorus determination and by paper chromatography. Cerium(III) chloride was prepared according to the method described by MOELLER and BRANTLEY[3]. The material was dissolved in water (with the aid of a small amount of hydrochloric acid) in order to get a stock solution which was 0·09 M in cerium. Its concentration was checked by precipitating cerium as oxalate and igniting the oxide.

Hydrochloric acid, sodium chloride and sodium hydroxide, used for adjusting pH and ionic strength values, were of analytical reagent quality.

[7] S. M. LAMBERT and J. I. WATTERS, *J. Amer. Chem. Soc.* **79**, 5606 (1957).
[8] J. I. WATTERS and S. M. LAMBERT, *J. Amer. Chem. Soc.* **81**, 3201 (1959).
[9] J. I. WATTERS, E. D. LOUGHRAN and S. M. LAMBERT, *J. Amer. Chem. Soc.* **78**, 4855 (1956).

Vol. 15 1960

Apparatus

All spectrophotometric measurements were made with a Beckman quartz spectrophotometer, Model DU, using fused silica cells with an optical light path of 1·000 ± 0·005 cm.

All pH measurements were made with the Beckman model G pH meter with the Beckman all purpose glass electrode and the Beckman reference electrode inserted directly in the solution.

Conductivity measurements were carried out with the aid of a line operated Conductivity Bridge, model RC-16B from the Industrial Instruments Inc., using platinized platinum electrodes immersed into the solution. The cell constant was not determined since conductance values were relative throughout a given titration.

Spectrophotometric measurements

Fig. 1 shows the curves obtained with $4{\cdot}5 \times 10^{-4}$ M cerium(III) chloride solutions to which sodium triphosphate was added in the ratio $Ce^{3+} : P_3O_{10}^{5-} = 1 : 4$. The ionic strength was adjusted to 0·3 with sodium chloride. In all cases, it is clearly observed that the cerium(III) spectrum is changed. The new absorption maximum which appears at 300 mμ at a low pH is slowly shifted to 304 mμ as the pH raises.

An inflexion at 255 mμ is also observed in solutions which have a low pH value but it disappears when the pH is higher than 4·0.

The new maximum which appears at 300–304 mμ is extensively influenced by the ratio of triphosphate ion to cerium(III) ion. When its value increases it is observed that for about the same values of pH the absorbance is higher. This tendency decreases as the pH increases. The ratio of triphosphate ion to cerium(III) ion has only a small influence on the maximum above the pH 7.0.

Method of continuous variations

The curves in Fig. 2, determining the composition of the soluble complex, were obtained by the method of Job[10]. See also Vosburgh and Cooper[11]. They refer to mixtures of solutions of cerium (III) chloride and sodium triphosphate of the same molar concentration but of different ratios of components.

Potentiometric titrations

The use of pH titration in this case can give useful information because of the pronounced hydrolysis of the triphosphate ion:

$$P_3O_{10}^{5-} + nH_2O \rightleftharpoons H_nP_3O_{10}^{5-n} + nOH^-$$

and by considering that cerium(III) behaves as an acid.

In Fig. 3 is presented the result of the potentiometric titration of a 0·09 M solution of cerium(III) chloride solution with sodium triphosphate solution of the same concentration. The precipitate which forms in the beginning of the titration is completely dissolved when the ratio of cerium(III) to triphosphate ions is about 1 : 1·5. The formation of a compound 1 : 1 is clearly observable, and no evidence for other compounds appears.

The results are not so evident with more dilute solutions although the 1 : 1 compound can still be observed. In very dilute solutions (9×10^{-4} M), the inflexion that corresponds to the previous compound was no longer evident, and a continuous line was obtained by plotting pH against the volume of sodium triphosphate solution. In no case could the soluble compound observed by the spectrophotometric procedure be detected by this means.

The reverse titration, i.e., sodium triphosphate by cerium(III) chloride solutions was less conclusive. Only continuous curves were observed and the formation of no particular compound could be detected.

Conductometric titrations

The titration of a 0·009 M cerium(III) chloride solution with a 0·09 M sodium triphosphate solution showed clearly the formation of two compounds: the normal cerium(III) triphosphate, $Ce_5(P_3O_{10})_3$, and one in which the ratio Ce(III) ions to triphosphate ions is 1 : 1 (Fig. 4). With more

[10] P. Job, *Ann. Chim.* (10) **9**, 113 (1928); (11) **6**, 97 (1936).
[11] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.* **63**, 437 (1941).

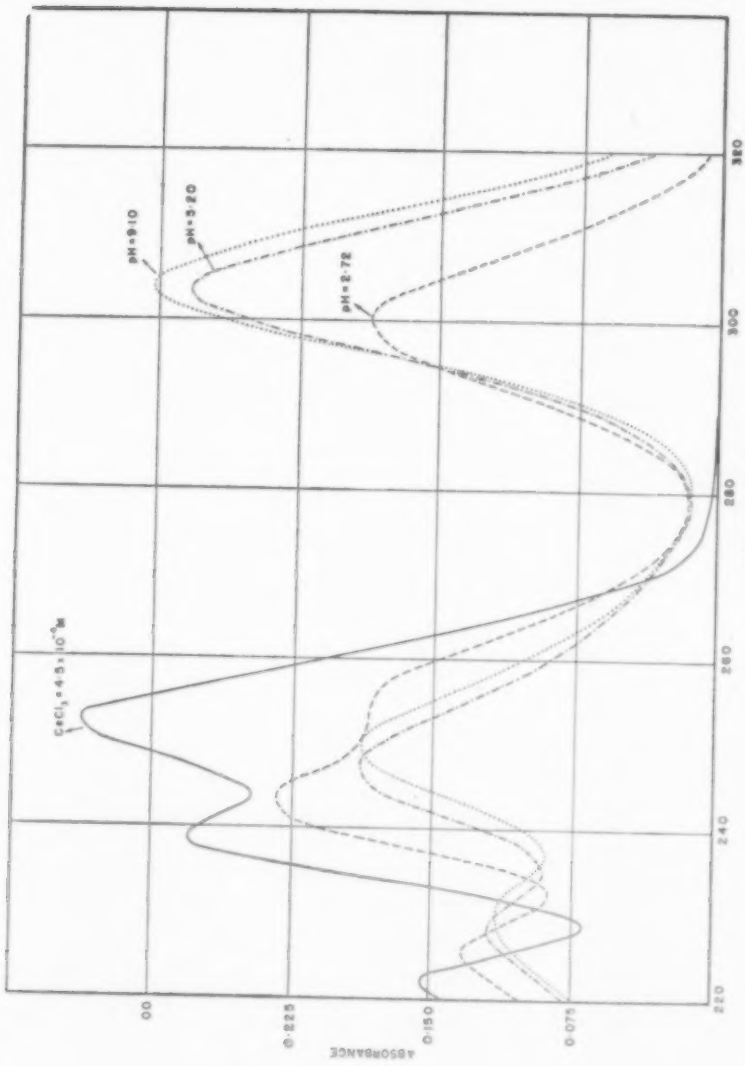

FIG 1.—Ultra-violet absorption spectra of a solution in which $Ce^{3+}:P_2O_{16}^{6-} = 1:4$, at various pH; $I = 0{\cdot}3$.

Vol. 15 1960

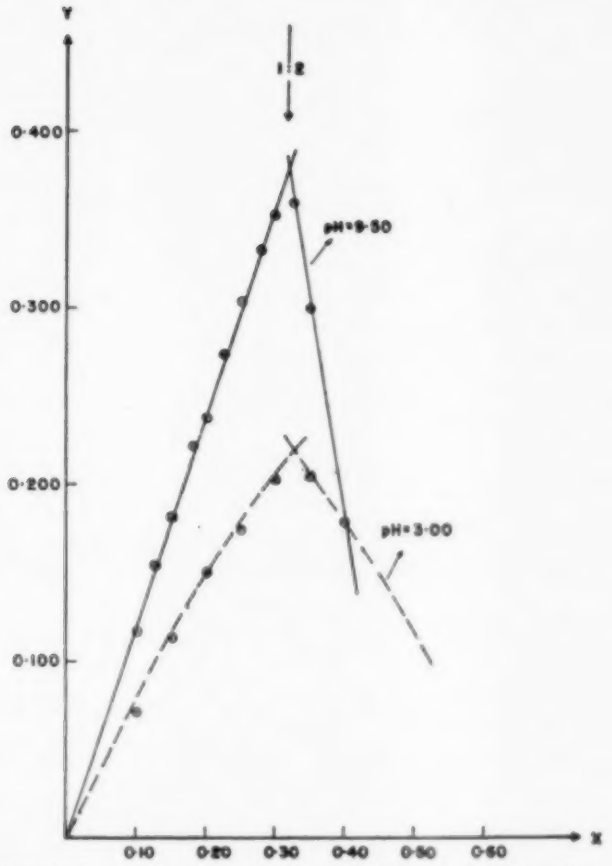

FIG. 2.—Method of continuous variation: cerium(III) chloride and sodium triphosphate mixtures at total concentration of $1{\cdot}8 \times 10^{-3}$ M; pH = 9·50 (= 304 mμ) and pH = 3·0 (= 300 mμ); $I = 0{\cdot}3$.

dilute solutions, the results were the same, and the formation of both compounds could be observed distinctly.

The inverse titration did not give good results. The formation of the compounds could not be observed as in the previous case.

Formation constant

An attempt was made to calculate the order of magnitude of the formation constant of the soluble complex $Ce^{3+} : P_3O_{10}^{5-} = 1 : 2$

By considering the equilibrium:

$$[CeNa_xP_3O_{10}]^{3-x} + P_3O_{10}^{5-} \leftrightharpoons [CeNa_x(P_3O_{10})_2]^{7-x}$$

and disregarding the concentrations of Ce^{3+} and $P_3O_{10}^{5-}$ from the dissociation of the 1 : 1 compound, the formation constant of the complex was calculated by a method closely similar to that described by TURNER and ANDERSON[12].

[12] S. E. TURNER and R. C. ANDERSON, *J. Amer. Chem. Soc.* **71**, 912 (1949).

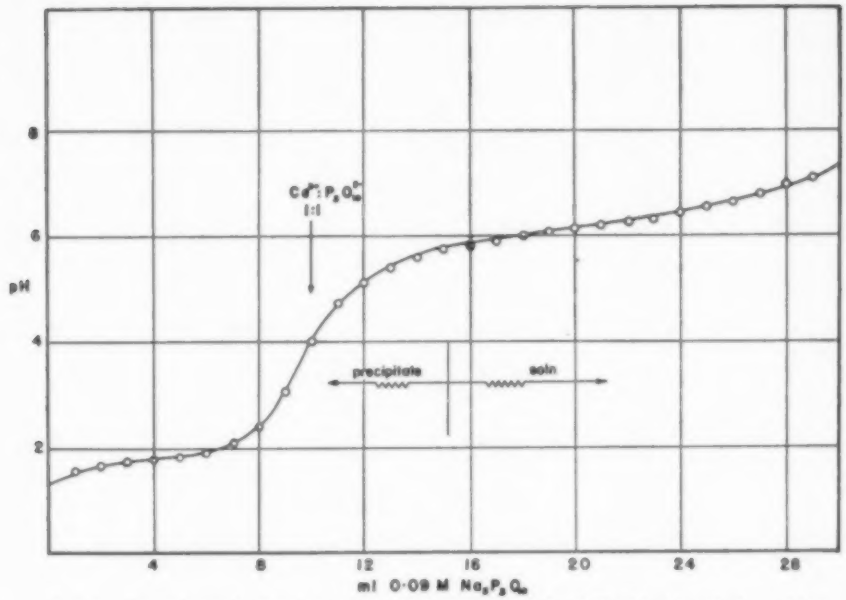

FIG. 3.—Potentiometric titration of 10 ml of a 0·09 M cerium(III) chloride solution with a 0·09 M sodium triphosphate solution.

Vol. 15 1960

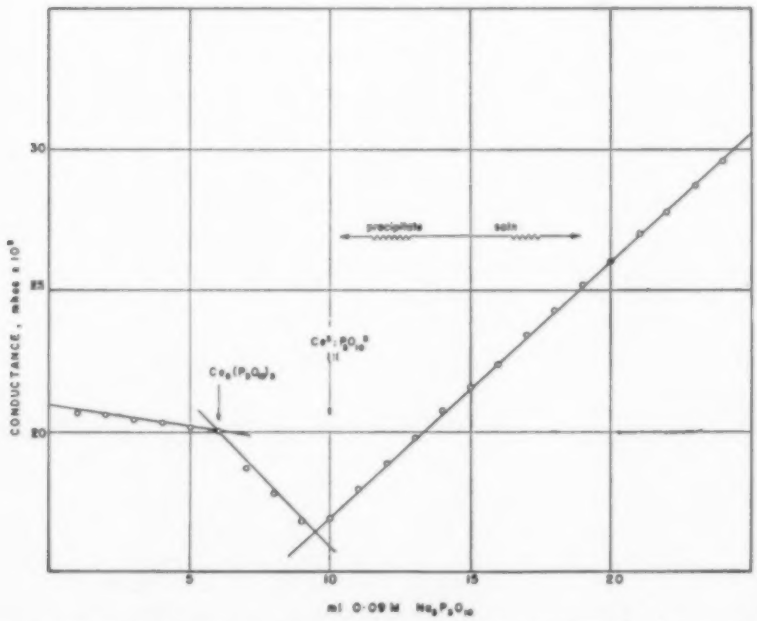

FIG. 4.—Conductometric titration of 100 ml of a 0·009 M cerium(III) chloride solution with a 0·09 M sodium triphosphate solution.

Pairs of solutions having equal optical density (and thus essentially equal concentrations of complex) but different concentrations of reagents were selected. Since the formation constant is the same for both members of a given pair, the concentration of complex and thus the value of K_2 may be calculated from the relation

$$K_2 = \frac{x}{(a_1 - b_1 - x)(b_1 - x)} = \frac{x}{(a_2 - b_2 - x)(b_2 - x)}$$

where the a's and b's represent initial concentration of triphosphate and cerium(III) ions respectively, and x the concentration of the complex formed.

So, $(b - x)$ represents the concentration of cerium(III) ion which is present as the (1 : 1) complex and $(a - b - x)$ represents the equilibrium concentration of triphosphate. There will be a decrease in free triphosphate concentration equal to b since every cerium ion is combined with at least one triphosphate; there will be a further decrease equal to x since every complex ion containing two triphosphates will remove another triphosphate ion.

Pairs of solutions with about the same optical density were selected from the measurements of the dilution curve obtained from the method of continuous variations. Cerium(III) and triphosphate ions practically do not show absorption at 304 mμ.

In one example the following values were selected:

$$a_1 = 0{\cdot}00135\ \text{M} \qquad a_2 = 0{\cdot}00117\ \text{M}$$

$$b_1 = 0{\cdot}00045\ \text{M} \qquad b_2 = 0{\cdot}00063\ \text{M}$$

$$I = 0{\cdot}3; \quad \text{pH} = 9{\cdot}50; \quad t = 25 \pm 1°\text{C}$$

The value of K_2 was found to be $7{\cdot}4 \times 10^3$. With two other pairs of solutions the values obtained for K_2 were respectively $8{\cdot}3 \times 10^3$ and $7{\cdot}8 \times 10^3$. By considering these three values, the mean value for K_2 is equal to $7{\cdot}5 \times 10^3$.

The constant calculated above was not corrected for the presence of sodium ions present in the solution.

Acknowledgements—The author wishes to express his gratitude to Dr. T. MOELLER and Dr. L. F. AUDRIETH of the University of Illinois, Urbana, Illinois, U.S.A. for helpful suggestions and encouragement and also to the Rockefeller Foundation and Conselho Nacional de Pesquisas (Rio de Janeiro) for the support given in the course of this investigation.

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SOME STUDIES ON VANADIC ACID

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Abstract—Results obtained in potentiometric and conductometric titrations using freshly-prepared vanadic acid have been compared. The results support the view that vanadic acid exists in solution as $H_6V_{10}O_{28}$. The reactions of the acid with poly-alcohols, hydroxy-acids and polyhydroxy-phenols are discussed. The reaction with hydrogen peroxide at various mole ratios had been studied by conductometric, potentiometric and spectrophotometric methods and compared with the reaction between peroxide and acidified vanadate solutions.

FORMULAE containing 2, 4, 5, 6, and 10 vanadium atoms have been suggested for isopolyvanadic acid.[1–9] The main evidence for such formulae has been derived from potentiometric and conductometric studies, in which points of inflexion or breaks in the curves have been reported at various Na:V ratios. Vanadic acid for such studies has usually been prepared by careful acidification of alkali vanadate or by dissolution of V_2O_5 in hydrogen peroxide followed by decomposition of the peroxide formed. Vanadic acid prepared by ion exchange has been used in some of the potentiometric studies of HAZEL *et al.*[6], and of SALMON and RUSSELL[10]; the experimental results were, however, interpreted differently. A recent potentiometric and spectrophotometric study in concentrated perchloric acid by ROSSOTTI and ROSSOTTI[8] has indicated the presence of an acid $H_6V_{10}O_{28}$, which forms ions $HV_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$. These ions are claimed to be the only ions present between pH 1·3 and 6·5.

It was felt of interest, therefore, to re-investigate the vanadic acid system using vanadic acid prepared by ion exchange. Both conductometric and potentiometric studies were made at several concentrations and the results compared.

Reactions of vanadic acid prepared by ion exchange with various hydroxy-organic compounds have also been studied.

EXPERIMENTAL

Vanadic acid solutions were prepared by passing a 0·1 M solution of AnalaR ammonium vanadate down a column containing sufficient ZeoKarb 225 (hydrogen form) to ensure complete exchange. A dark band between the ammonium band and the hydrogen band indicated the degree of exhaustion of the resin, and was not allowed to travel more than half-way down the column. This band consists of vanadium in a reduced form and is easily removed on regeneration of the column with acid. Since the acid is readily precipitated from concentrated solutions, only small quantities were prepared with a small column of capacity~30 mequiv. All studies were made on freshly prepared acid.

[1] L. P. DUCRET, *Ann. Chim.* **6**, 705 (1951).
[2] P. DÜLLBERG, *Z. Physik. Chem.* **45**, 129 (1903).
[3] G. CARPENI and P. SOUCHAY, *J. Chim. Phys.* **42**, 149 (1945).
[4] P. TRUJILLO, *An. Fis. Quim. Madrid* **50B**, 553 (1954).
[5] H. T. S. BRITTON and R. A. ROBINSON, *J. Chem. Soc.* 1261 (1930).
[6] J. F. HAZEL, W. M. MCNABB and R. SANTINI, *J. Phys. Chem.* **57**, 681 (1953).
[7] G. JANDER and K. JAHR, *Z. Anorg. Chem.* **212**, 1 (1933).
[8] F. J. C. ROSSOTTI and H. ROSSOTTI, *Acta Chem. Scand.* **10**, 957 (1956).
[9] P. SOUCHAY and F. CHAUVEAU, *C. R. Acad. Sci., Paris* **244**, 1923 (1957).
[10] R. U. RUSSELL and J. E. SALMON, *J. Chem. Soc.* 4708 (1958).

Vol. 15 1960

pH Measurements were made with a Cambridge pH-meter and a glass-calomel electrode system. Conductivity measurements were made with a Mullard Conductivity Bridge, operating in the most sensitive range, with a cell constant of 1·54. Spectrophotometric measurements were made on a Unicam S.P. 500 with 1 cm cells; appropriate blank solutions were used. All experiments were conducted at 18°C.

Vanadium was determined colorimetrically using an acidified solution with hydrogen peroxide; all solutions (including standards) were boiled with 5 ml 2 N NaOH, cooled, boiled with 10 ml 2 N H_2SO_4, cooled again, and were then treated with 10 ml 0·4 M peroxide and diluted to 50 ml. Analysed AnalaR ammonium vanadate, NH_4VO_3 (minimum content 98·5), per cent was used as a primary standard. This procedure was found to be superior to that usually employed by other authors;[9,10]

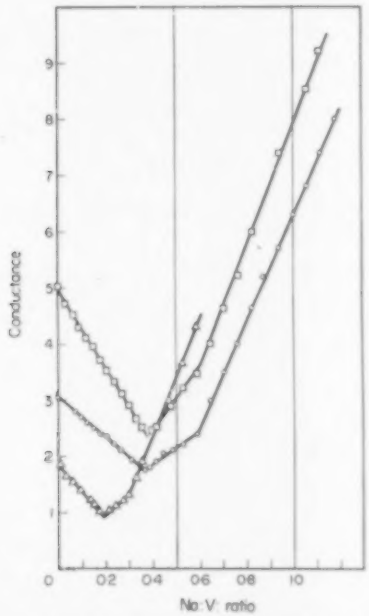

FIG. 1.—Conductrometric titration of vanadic acid with NaOH. ○ Titration of 20 ml vanadic acid with N.NaOH. Conductance, $10^{-3}\Omega^{-1}$; △ titration of 10 ml vanadic acid + 10 ml H_2O N.NaOH. Conductance, $10^{-3}\Omega^{-1}$; □ titration of 2 ml vanadic acid + 18 ml H_2O with 0·1 N NaOH. Conductance, $10^{-4}\Omega^{-1}$.

moreover small aliquots were sufficient for accurate determination. Hydrogen peroxide solutions were prepared from unstabilized 20 volume peroxide kindly supplied by Laporte Chemicals Ltd., and were standardized in acid solution (H_2SO_4) against 0·1 N $KMnO_4$.

RESULTS AND DISCUSSION

(a) *Titration studies on vanadic acid*

The results obtained on conductometric titration of three samples of vanadic acid at different concentrations are shown in Fig. 1. These were obtained by adding an aliquot of sodium hydroxide, shaking, then allowing the mixture to stand for 2 min before reading. Separate experiments were performed at various Na:V ratios where the conductance was read immediately and again after several weeks. Comparison of the results showed that whilst the first section of the curves was unaltered, a considerable fall in conductance and displacement of the curve to higher Na:V ratios occurred in the third section. It is obvious from Fig. 1, however, that immediate

titration gives breaks at Na:V ratios of 0·38:1 and 0·6:1. The actual value of the former ratio varies somewhat with the concentration of the solution but is sensibly 0·4:1.

Potentiometric titration of a similar aliquot with N.NaOH is shown in Fig. 2 (Curve a). Comparison of this curve with Fig. 1 shows that points of inflexion occur at Na:V ratios corresponding to the break-points in the conductometric curves. In addition, however, a sharp break occurs at ~0·5:1. This latter break, or point of

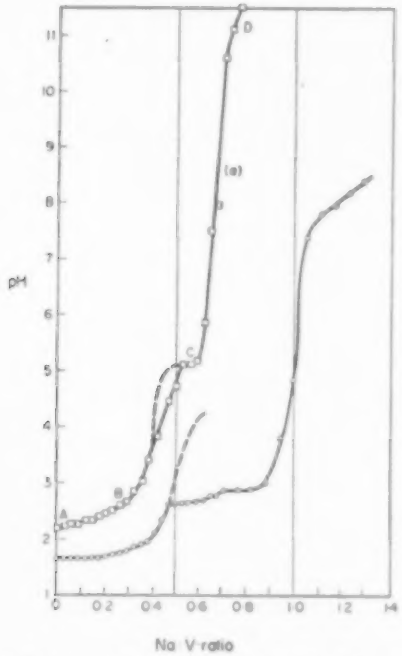

FIG. 2.—Potentiometric titration of vanadic acid with N. NaOH. □ 20 ml vanadic acid +20 ml H_2O; ○ 20 ml vanadic acid +20 ml H_2O_2.

inflexion has also been found by SALMON and RUSSELL[10] and by SOUCHAY and CHAUVEAU[9], by potentiometric titration and has been interpreted in terms of a hexavanadate ion $(HV_6O_{17})^{3-}$.

The results of both experiments appear to be best interpreted in terms of a decavanadic acid as suggested by ROSSOTTI and ROSSOTTI[5]. The first break in the conductance curve at an Na:V ratio of 0·38:1 then corresponds to the reaction

$$H_6V_{10}O_{28} + 4NaOH \rightarrow Na_4H_2V_{10}O_{28} + 4H_2O \quad (1)$$

The second stage

$$Na_4H_2V_{10}O_{28} + NaOH \rightarrow Na_5HV_{10}O_{28} + H_2O \quad (2)$$

is not indicated directly by either curve, but the completion of the third stage

$$Na_5HV_{10}O_{28} + NaOH \rightarrow Na_6V_{10}O_{28} + H_2O \quad (3)$$

is indicated on both conductance and pH curves. The shape of the pH curve over the region BC does, however, indicate a continuous shift of equilibrium during this stage.

Vol. 15 1960

The anticipated shape of the curve in the absence of (2) is indicated by a broken line. It is obvious, therefore, why many authors, in the absence of conductance data, have drawn different conclusions from the shape of the pH curves, in particular at a Na:V ratio of 1:2. Whilst it is not impossible that the ion $(HV_6O_{17})^{---}$ is formed at equilibrium (indeed, the shape of the equilibrium curves obtained by SALMON[10] and other workers support this concept), it appears very doubtful whether this ion is formed during the initial titration.

Although vanadic acid prepared by ion exchange is unstable in concentrated solutions (~0·05 M V), forming precipitates of hydrated vanadium pentoxide, there is no reason to suppose, as suggested by other authors,[6] that a low molecular weight acid $H_6V_{10}O_{28}$ is in equilibrium with a higher molecular weight material. Unfortunately these authors give no details of the type of resin, the age of the acid or the method of analysis for vanadium, thus making reinterpretation of their data difficult. In the present work with freshly-prepared vanadic acid no evidence has been found for the presence of colloidal material, and all the vanadium present in a freshly-prepared solution can be accounted for in terms of the simple titration data presented in Figs. 1 and 2. Dilute sodium chloride solution does not cause immediate precipitation.

(b) *Some reactions of vanadic acid*

Molybdic and tungstic acids prepared by ion exchange form complexes with tartaric and other hydroxy-acids of greater acid strength.[11] A similar investigation with vanadic acid using conductometric and spectrophotometric techniques gave no evidence for compound formation, and addition of tartaric acid appeared to have no effect on the acid strength. The effect of poly-alcohols and sugars on vanadic acid is dependent on the concentrations employed. Vanadic acid (0·11 M) was reduced by glucose, mannitol and erythritol (0·3 M) to form green precipitates. In dilute solution (0·04 M V) these compounds had no effect on the conductance of vanadic acid. Penta-erythritol was the only material which showed evidence of complex formation; a 0·3 M solution raised the conductance 20 per cent, prevented precipitation of vanadic acid (0·15 M) and produced a deep red coloration.

Polyhydroxy phenols (gallic acid, pyrogallol and catechol) also showed some evidence of complex formation, but the complexes were so readily oxidized that attempts to determine their formulae by the method of continuous variations led to in most experiments irreproducible results. Moreover, solutions of vanadic acid, even in excess polyhydroxy-phenol, do not obey Beer's Law. Satisfactory data were ultimately obtained for gallic acid and pyrocatechol, which appeared to form complexes having ratios of 1 V:2 gallic acid and 1 V:pyrocatechol. Mixtures of vanadic acid (0·02 M) and molybdic acid (0·04 M) in various mole ratios showed no tendency to react to form stronger acids. A continuous rise in conductance and fall in density of colour was found as the fraction of molybdic acid in the mixture was increased. Molybdic acid appeared to stabilize the vanadic acid since no precipitation occurred in the samples containing molybdic acid.

The effect of hydrogen peroxide on vanadates at various Na:V ratios has been extensively studied,[12] but little work has been reported on the reaction with free

[11] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **13**, 84 (1960).
[12] F. CHAUVEAU, Thesis, Paris (1959).

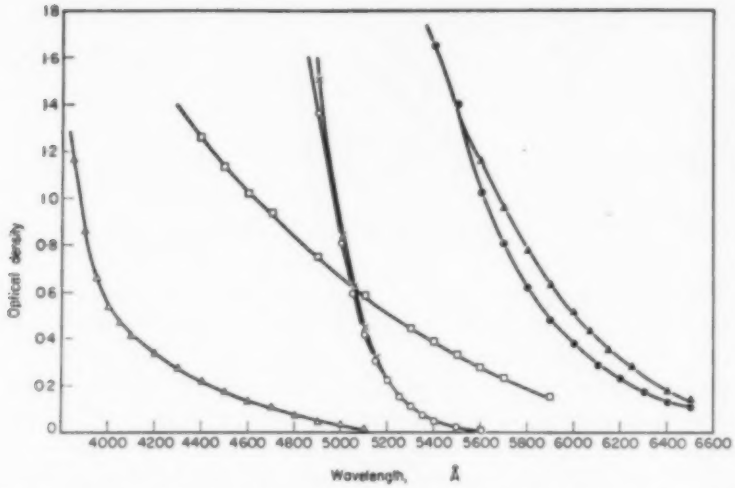

FIG. 3.—Spectra of vanadate solutions. △ Ammonium vanadate 0·05 M; × ammonium vanadate 0·05 M in 0·05 M $HClO_4$; ○ freshly prepared vanadic acid 0·045 M; ▲ 0·045 M vanadic acid in 0·045 M H_2O_2. Reaction noticeable after 5 min. Spectrum taken after ~15 min when intensity still increasing. ● 0·04 M ammonium vanadate in 0·04 M H_2O_2 pH adjusted to 1·8 with $HClO_4$; □ 0·01 M ammonium vanadate in 0·01 M H_2O_2 pH adjusted to 2·25 with $HClO_4$.

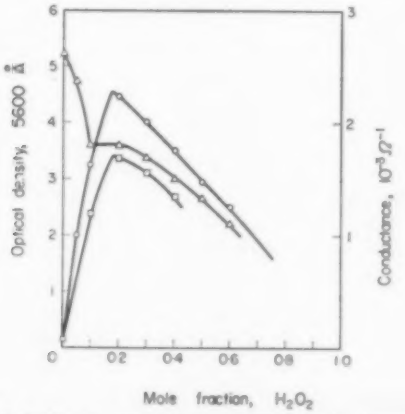

FIG. 4.—The effect of hydrogen peroxide on vanadic acid prepared by ion-exchange. △ Conductance of solutions after 3 hr. Both solutions 0·07 M; ○ optical density of solutions after 2½ hr; □ optical density of solutions after 3 hr.

vanadic acid. BELTRAN and TRUJILLO[13] dissolved V_2O_5 in hydrogen peroxide but found the reaction complicated, and suggested that an unstable perpyrovanadic acid $H_4V_2O_4(O_2)_3$ was formed in solution. According to REMY[14] the acid formed is $H_3[VO_2(O_2)_2]$. The use of vanadic acid should simplify the study but also yields complicated results (Figs. 2–6). Addition of a small quantity of peroxide ($V:H_2O_2$ ratio 1 : 0·5) decreased the conductance and produced an intense red-brown coloration. Increasing the ratio to 1:1 initially caused an increase in conductance to $0{\cdot}46 \times 10^{-2}$

[13] J. BELTRAN and R. TRUJILLO, *An. Fis. Quim. Madrid* **47B**, 699 (1951).
[14] H. REMY, *Treatise on Inorganic Chemistry* Vol. 2. Elsevier, New York (1956).

Vol. 15 1960

Ω^{-1} and only a slight change in colour; on standing, however, the conductance fell to $0{\cdot}155 \times 10^{-2}\Omega^{-1}$ as before, and the solution became red-brown. At a ratio of 1:2 the conductance increased to three times its original value and the pH decreased from 2·18 to 1·66. The red-brown colour only formed in these solutions after several hours in the absence of additives but appeared more rapidly on adding NaOH; it is itself un-

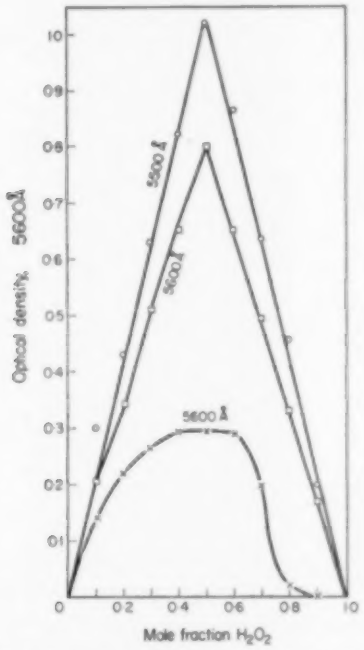

FIG. 5.—The effect of hydrogen peroxide on ammonium vanadate acidified with H_2SO_4 and $HClO_4$. (a) NH_4VO_3 0·025 M; (b) H_2O_2 0·025 M ×20 ml (a) + (b) + calculated quantity of 0·1 N $HClO_4$ equivalent to NH_4VO_3 then 3 ml excess. Total volume made to 30 ml with H_2O. pH values between 2·00–2·20. □ 20 ml (a) + (b) + 5 ml 4·5 N $HClO_4$. Total volume made to 30 ml with H_2O; ○ 20 ml (a) + (b) + 5 ml 2N H_2SO_4. Total volume 25 ml.

stable, however, and gradually decreases in intensity after a certain time. In an attempt to determine the formula of the red-brown complex a series of H_2O_2-vanadic acid mixtures were prepared in various mole ratios using JOB's[15] method. The maximum optical density was then measured at 5600 Å, where other species do not interfere appreciably (Figs. 3 and 4). From Fig. 4 it appears that the complex is formed at a ratio of V:O = 4:1. Although the intensity of the colour varies with time the position of the maximum remains constant. The pH at the maximum was 2·30. For comparison, a similar series of mixtures was prepared from ammonium vanadate and hydrogen peroxide, a calculated quantity of $HClO_4$ being added to each tube to bring the pH to approximately the same value (actually 2·2). The results in this case were quite different (Fig. 5), a maximum occurring at V:O = 1:1 but the colour and spectrum obtained were similar. Addition of excess acid to a second series of tubes produced a maximum at the same ratio but the intensity of the colour was increased

[15] P. JOB, *Ann. Chim.* **6**, 97 (1935).

considerably. Excess sulphuric acid produced similar results. A red-brown cation of formula $(VO_2O)^+$ has been postulated by CHAUVEAU and SOUCHAY[16] in acid solution, from pH studies,

$$(VO_3 2O)^- + 2H^+ \rightleftharpoons (VO_2O)^+ + H_2O_2$$

The shape of the curve in Fig. 5 indicates that $(VO_2O)^+$ is formed quantitatively in excess strong acid, but that formation of yellow $(VO_3 2O)^-$ occurs in more dilute

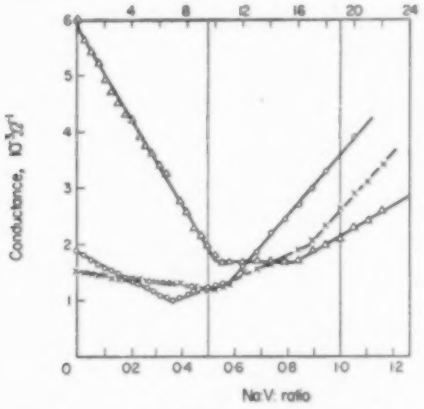

FIG. 6.—Conductometric titration of peroxide-vanadic acid mixtures. ○ 20 ml vanadic acid +20 ml H_2O versus N. NaOH; × 20 ml vanadic acid +15 ml H_2O + 5 ml H_2O_2 (0·17 M) versus N. NaOH; △ 20 ml vanadic acid +20 ml H_2O_2 (0·17 M) versus N. NaOH.

acid at higher O:V ratios. It appears probable from these results and a comparison of the absorption spectra (Fig. 3) that the red-brown species formed in dilute peroxide solutions of vanadic acid prepared by ion exchange is $(VO_2O)^+$. The displacement of the curve to lower O:V ratios (Fig. 4) may be best explained by an equation of the type

$$aH_6V_{10}O_{28} + bH_2O_2 \rightarrow (VO_2O)_x(V_{10}O_{28}H_z)_y$$

Interpretation of the titration curves (Figs. 2 and 6) in excess peroxide is difficult in the absence of further data, but it is clear from the shape of the curves that a strong peroxy-acid is formed initially.

Further studies are being made at present in an attempt in an attempt to determine the structure of the peroxy ions in solution; the results will be reported later.

[16] F. CHAUVEAU and P. SOUCHAY, *C. R. Acad. Sci., Paris* **245**, 1334 (1957).

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 279 to 286. Pergamon Press Ltd.

EFFECT OF TRANSITION METAL ION ON RATES OF HYDROGEN EXCHANGE IN METAL AMMINES

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(*Received* 30 *December* 1959)

Abstract—The rate of hydrogen exchange of metal ammines decreases with increasing atomic number of the metal for a given family of elements. For iso-electronic systems the rate increases markedly with increasing charge of the metal ion. Square complexes exchange more rapidly than do octahedral ammines of neighbouring metals. These results are discussed in terms of the crystal (ligand) field theory of bonding for transition metal complexes.

KINETIC investigations of base catalysed hydrogen exchange of metal ammines in aqueous solution were first reported by ANDERSON and co-workers.[1] They observed that the rates of hydrogen exchange decrease in the order $Co(en)_3^{3+} > Co(NH_3)_6^{3+} > Pt(NH_3)_4^{2+}$ and that the $Pd(NH_3)_4^{2+}$ system was complicated by the ease of Pd-N bond cleavage. BLOCK and GOLD[2] report that $Co(NH_3)_4C_2O_4^+$ exchanges hydrogen more slowly than does $Co(NH_3)_6^{3+}$. It was found for all of these cases that the rate of hydrogen exchange is specific hydroxide ion catalysed.

Recent studies[3] show that either near infra-red or nuclear magnetic resonance measurements can be used to conveniently follow the rates of hydrogen exchange in metal ammines. Making use of infra-red measurements, it has been possible to study a large number of different metal complexes. This paper reports some results of such an investigation and makes an attempt to account for the effect of the central metal ion on the rates of hydrogen exchange.

EXPERIMENTAL

Preparation of compounds. All of the compounds used in this study are known compounds and were prepared by the methods described in the literature.[4] Each compound was characterized by analysis for one or more elements and in some cases also by a comparison of absorption spectrum with that of the known compound. The compound $[Os(NH_3)_5]Br_3$ was generously given to us by Professor G. W. WATT, whilst the compound $[Ru(NH_3)_6]Cl_3$ was purchased from Johnson and Matthey Ltd., 78–83 Hatton Garden, London.

Determination of hydrogen exchange rates. The method used to follow the rate of hydrogen exchange in these systems is the same as that described previously.[3] Briefly, it involves measurements of optical density at 1·65 μ to determine the increase in OH concentration with time for a reaction mixture originally containing a hydrogen–1 metal ammine in an acetate buffered heavy water solution. The buffer solution was prepared by adding anhydrous sodium acetate and acetic anhydride to 99·5% D_2O to give 0·1 M $NaC_2H_3O_2$ and 0·1 M $DC_2H_3O_2$. Measurements were made with a Beckman Model DK-2 recording spectrophotometer which was equipped with a cell holder maintained at constant temperature (±0·1°C) by circulating water through it from a thermostatted water-bath.

[1] J. S. ANDERSON, H. V. A. BRISCOE and N. F. SPOOR, *J. Chem. Soc.* 361 (1943). J. S. ANDERSON, H. V. A. BRISCOE and L. COBB, *Ibid.* 367 (1943).
[2] H. BLOCK and V. GOLD, *J. Chem. Soc.* 966 (1959).
[3] J. W. PALMER, F. BASOLO and R. G. PEARSON, *J. Amer. Chem. Soc.* **82**, 1073 (1960).
[4] For methods of syntheses see appropriate volumes of *Gmelin's Handbuch der anorganischen Chemie*. Verlag Chemie, Berlin.

The rates of hydrogen exchange were determined by plotting log $(H_\infty - H_t)$ vs. t where H_∞ is the optical density at infinite time and H_t is the optical density at time t. The product of the slopes of these curves and $-2{\cdot}3$ gave the pseudo first order rate constant, k_{obs}, which when divided by $[OD^-]$ gave the reported second order rate constants, k. The values of k were determined with a precision of 15 per cent. The $[OD^-]$ calculated on the basis of a pK_a of 5·26 for $DC_2H_3O_2$ and a K_i for D_2O[5] of $0{\cdot}15 \times 10^{-14}$ was adjusted in each case for the small (never more than 0·2 pH units) variation in pH resulting from the addition of the complex to acetate buffered H_2O solutions.[6]

Acid strengths of $M(NH_3)_5H_2O^{3+}$. The acid strengths of $Co(NH_3)_5H_2O^{3+}$ and $Ir(NH_3)_5H_2O^{3+}$ were determined by titrating 1×10^{-3} M solutions of the complexes with 0·0276 M NaOH at 25°C. Titrations were made using a Beckman model G glass electrode pH meter, calibrated with buffers at pH 7·0 and 4·0. Correction to an ionic strength of zero was made using the equation

$$\log K_a = \log K_0 + 2\sqrt{u} + u.$$

Linear plots of $\log [M(NH_3)_5OH^{2+}]/[M(NH_3)_5H_2O^{3+}]$ vs. pH were obtained showing that the complexes do not decompose during titration.

Infra-red spectra. The infra-red absorption spectra were measured in the rock salt region with a Baird Model AB-2 double beam recording spectrophotometer. Measurements were made on solid compounds using the KBr wafer technique and each spectrum was calibrated by comparison to a superimposed polystyrene spectrum.

RESULTS AND DISCUSSION

Previous investigators have found that the observed rate constant for hydrogen exchange of metal ammines does not depend upon the concentration of the complex but is inversely dependent upon the hydrogen ion concentration. This was checked and confirmed for these studies in D_2O as a solvent rather than H_2O. Thus the data in Table 1 show that within experimental error, the second order rate constant k is not

Vol. 15 1960

TABLE 1.—EFFECT OF CONCENTRATION OF COMPLEX AND OF ACETATE ON HYDROGEN EXCHANGE RATE OF METAL AMMINES IN $DC_2H_3O_2$–$C_2H_3O_2^-$ BUFFER

Complex*	Concentration†	Temp.(°C)	$k \times 10^{-4}(M^{-1}\ sec^{-1})$
$Co(NH_3)_6^{3+}$	0·22 M	29·9	2·6
$Co(NH_3)_6^{3+}$	0·11	29·9	2·5
$Co(NH_3)_6^{3+}$	0·11(0·02 M $C_2H_3O_2^-$)‡	29·9	3·0
$Rh(en)_3^{3+}$	0·17	25·0	0·22
$Rh(en)_3^{3+}$	0·42	25·0	0·20

* en = $NH_2CH_2CH_2NH_2$.
† Concentration represents that of complex.
‡ Buffer ratio always one and concentration 0·1 M except in this case.

affected by changes in concentration of the complex or of acetate ion. Further evidence that the acetate ion makes little or no contribution to the rate of hydrogen exchange is supported by plots of k_{obs} vs. $[OD^-]$ shown in Fig. 1. At constant acetate ion concentrations such curves are expected to extrapolate to an intercept corresponding to the numerical value of acetate ion catalysis, since

$$k_{obs} = k_{OD^-}[OD^-] + k_{OAC^-}[OAC^-].$$

The intercept values are almost zero indicating a contribution from acetate ion of less than $10^{-3}\ M^{-1}\ sec^{-1}$.

[5] S. KORMAN and V. K. LAMER, *J. Amer. Chem. Soc.* **58**, 1403 (1936). R. KINGERLEY and V. K. LAMER, *Ibid.* **63**, 3260 (1941).
[6] L. H. COBB and J. S. ANDERSON, *Trans. Faraday Soc.* **40**, 145 (1943).

Investigations that show a specific hydroxide ion catalysis of hydrogen exchange in metal ammine are usually made over a rather limited acid buffer region. This has been necessary because in alkaline solutions the exchange would be much too fast to study by the conventional techniques used. However, by means of a line broading nuclear

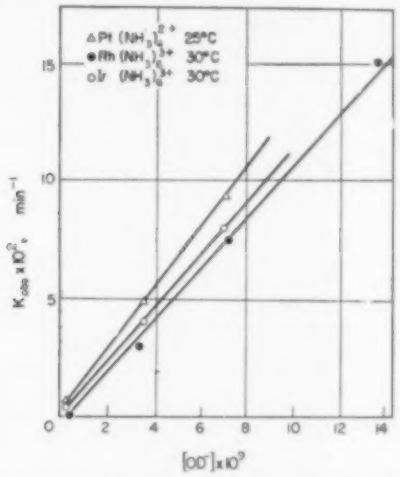

FIG. 1.—Rates of hydrogen exchange of metal ammines in $DC_2H_3O_2$–$C_2H_3O_2$ buffers as a function of OD^- concentration.

TABLE 2.—RATES OF HYDROGEN EXCHANGE OF METAL AMMINES IN 0·1 M $DC_2H_3O_2$–$C_2H_3O_2^-$ BUFFER AT 25°C

Complex	$k \times 10^{-6}(M^{-1}\ sec^{-1})$	Complex	$k \times 10^{-6}(M^{-1}\ sec^{-1})$
$Co(NH_3)_6^{3+}$	1·6	$Co(en)_3^{3+}$	2·4
$Rh(NH_3)_6^{3+}$	0·21	$Rh(en)_3^{3+}$	0·22
$Ir(NH_3)_6^{3+}$	0·015	$Ir(en)_3^{3+}$	0·02†
$Cr(NH_3)_6^{3+}$	2·6	$Cr(en)_3^{3+}$	3·6
$Ru(NH_3)_6^{3+}$	600	$Os(en)_3^{3+}$	~6‡
$Os(NH_3)_6^{3+}$	6	$Os(en)_3^{4+}$	Inst ($pK_a = 5·8$)[8]
$Pt(NH_3)_6^{4+}$	Inst. ($pK_a = 7·9$)[8]	$Pt(en)_3^{4+}$	Inst ($pK_a = 5·5$)[8]
$Pd(NH_3)_4^{2+}$	100*	$Pd(en)_2^{2+}$	1·5
$Pt(NH_3)_4^{2+}$	0·48	$Pt(en)_2^{2+}$	0·16
		$Au(en)_2^{3+}$	Inst($pK_a \sim 6·5$)[10]

* This value is high due to lability of the complex. See discussion in last paragraph of text.
† Estimated on the basis of a value of $2 \times 10^6 M^{-1}\ sec^{-1}$ at 48·5°C and K_a of $Ir(NH_3)_6^{3+}$.
‡ Estimated to be similar to $Os(NH_3)_6^{3+}$ since values of other $M(NH_3)_6^{3+}$ and $M(en)_3^{3+}$ are comparable.

magnetic resonance technique, the rates of hydrogen exchange of $Cr(NH_3)_6^{3+}$ and of $Cr(en)_3^{3+}$ in 0·022 M NaOH were recently determined.[7] The values of k are $2·5 \times 10^6\ M^{-1}\ sec^{-1}$ and $3·7 \times 10^6$ at 25°C respectively compared to $2·6 \times 10^6$ and $3·6 \times 10^6$ obtained in acetate buffers (Table 2). These results nicely show that the hydroxide ion dependence is first order over a very large concentration range. However, some

[7] R. G. PEARSON, J. W. PALMER, M. M. ANDERSON and A. L. ALLRED, *Z. Elecktrochem.* **64**, 110 (1960).
[8] A. A. GRINBERG and K. I. GIL'DENGERSHEL, *Izv. Akad. Nauk SSSR* 479 (1948).
[9] F. P. DWYER and J. W. HOGARTH, *J. Amer. Chem. Soc.* **77**, 6152 (1955).
[10] B. P. BLOCK and J. C. BAILAR, JR., *J. Amer. Chem. Soc.* **73**, 4722 (1951).

evidence has also been found for general base catalysis. Thus for $Cr(en)_3^{3+}$* in an en–HCl buffer at pH 9·8, the rate constant estimated for the ethylenediamine catalysed exchange is 2×10^2 M^{-1} sec^{-1}. Evidence was likewise obtained for water catalysis of hydrogen exchange with the complex *trans*- $Pt(en)_2Cl_2^{2+}$ of acid strength[8] pK_a = 10·4. Rates of exchange in 0·1 and 0·01 M HCl are approximately the same. Calculated on the basis of OD^- catalysis, the second order rate constants are approximately 1×10^{12} M^{-1} sec^{-1} which cannot be correct because this would be faster than a diffusion controlled process. On the basis of D_2O catalysis values of 7×10^{-3} and 10×10^{-3} M^{-1} sec^{-1} respectively at 25°C are obtained. These results support a general base catalysis and suggest the apparent specific hydroxide ion effect is simply the result of a large value of β in the Bronsted relationship $k_B = GK_B^{\beta}$, between rate constant, k_B and base dissociation constant K_B.*

TABLE 3.—TEMPERATURE DEPENDENCE OF HYDROGEN EXCHANGE OF METAL AMMINES

Complex	E_a, kcal *	$\Delta S_{25}^{\ddagger}$ (e.u.)
$Co(NH_3)_6^{3+}$	14 ± 1	14
$Rh(NH_3)_6^{3+}$	15 ± 2	13
$Ir(NH_3)_6^{3+}$	23 ± 2	34
$Cr(NH_3)_6^{3+}$	12 ± 2	8
$Pt(NH_3)_4^{2+}$	11 ± 1	2

* The E_a values reported here are 14·4 kcal smaller than the experimental values obtained by plotting log k_{obs} against $1/T$. This correction is necessary to compensate for the heat of ionization of the solvent.[12]

Vol. 15 1960

Data in Tables 2 and 3 afford a comparison of the rates of hydrogen exchange of metal ammines as a function of the kind of metal ion. It is convenient to discuss these results in terms of (1) family trends, (2) charge of the metal (3) electronic configuration of the metal and (4) co-ordination number.

(1) *Family trends.* The best example of this is given by the cobalt triad where it is seen that the ratio of rates of reaction for $M(NH_3)_6^{3+}$ where $M^{3+} = Co^{3+}$, Rh^{3+} and Ir^{3+} is approximately 100 : 15 : 1. Such a result was most unexpected, since the stability of these ammines are believed to increase with increasing atomic number. Thus a greater Ir–N bond strength is expected to result in a weaker N–H bond and therefore a more acid ammine. In fact ANDERSON *et al.* had suggested that the hydrogen exchange of $Co(en)_3^{3+}$ is faster than that of $Co(NH_3)_6^{3+}$ because the ethylenediamine complex is the more stable.

These apparently anomalous results can be explained on the basis of the crystal (ligand) field theory[11] of bonding in transition metal complexes. Consider that the transition state for hydrogen exchange of ammine approximates that of an amido-ammine, e.g. $[(NH_3)_5MNH_2 \cdots H \cdots OD]^{2+}$. Therefore, as the crystal field strength of NH_2 is less than that of NH_3, it follows that systems with large crystal field stabilization energies (CFSE) such as $Ir(NH_3)_6^{3+}$ will be less acidic than if CFSE were not a

* Another possible explanation is based on the fact that hydroxide can form an ion-pair with the complex.[2,3]

[11] F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions* Chap. 2. John Wiley, New York (1958).

factor. Likewise the activation energy for hydrogen exchange would be greater because of the loss of CFSE in converting NH_3 into "NH_2" in the transition state. Data in Table 3 show that the activation energies for the hexammines of Co^{3+}, Rh^{3+} and Ir^{3+} are 14, 15 and 23 kcal/mole respectively.

Assuming that this difference is at least in part due to crystal field effects, it is of interest to estimate the loss of CFSE in going from $M(NH_3)_6^{3+}$ to $M(NH_3)_5NH_2^{2+}$. This can be approximated using data provided by JØRGENSEN[12]. Thus the relative crystal field strengths for a given ligand for the following metals are: Co^{3+}, 1·0; Rh^{3+}, 1·54; Ir^{3+}, 1·90; Pt^{4+}, 2·1. The crystal field transition d_{xy}, d_{yz}, $d_{xz} \rightarrow$ lowest singlet of d_{z^2} or $d_{x^2-y^2}$ corresponds to approximately 43,000 cm^{-1} for $Pt(NH_3)_6^{4+}$ and 34,000 cm^{-1} for $Pt(NH_3)_5NH_2^{3+}$, or a difference of 9000 cm^{-1}. Since two of the *d* orbital electrons are raised in energy by pd–π bonding with *p* orbital electrons of the amido group, the maximum loss in CFSE for $Pt(NH_3)_6^{4+} \rightarrow Pt(NH_3)_5NH_2^{3+}$ is $9{,}000 \times 2 = 18{,}000$ cm^{-1} (1000 cm^{-1} = 2·86 kcal.) or 51 kcal. From the relative crystal field stabilization ratios given above, corresponding estimates in loss of CFSE are 24, 37 and 46 kcal/mole for the hexammines of Co^{3+}, Rh^{3+} and Ir^{3+} respectively. The activation energies are much smaller than this as is to be expected because the amido group is not completely formed in the transition state. Likewise other factors may contribute to the activation energies.

Although the activation energies for hydrogen exchange for the hexammines of the cobalt triad increase in the same order as do the losses in CFSE, it must be admitted that the correlation is not entirely satisfactory. Note that the estimates of CFSE suggest roughly an average value for $Rh(NH_3)_6^{3+}$ but instead its activation energy is only slightly larger than that of $Co(NH_3)_6^{3+}$ and much smaller than the value obtained for $Ir(NH_3)_6^{3+}$. One possible explanation might be that the activation energy for $Ir(NH_3)_6^{3+}$ is unusually large because of attractive interaction between the ammine hydrogens and the non-bonding *d*- electrons of Ir^{3+}. Evidence is cited in support of such interaction in Pt^{2+} complexes but a much smaller effect is expected for Pd^{2+} and Ni^{2+} systems.[14]

The acid strengths of the hexammines of Co^{3+}, Rh^{3+} and Ir^{3+} are not known but the pK_a values for $M(NH_3)_5H_2O^{3+}$ are 5·7, 5·9 and 6·1* respectively.[15] This decrease in acid strength correlates the decrease in rates of hydrogen exchange but the effect is very small. The slower rate of exchange of $Ir(NH_3)_6^{3+}$ is also in agreement with its N–H stretching frequency being approximately 20 cm^{-1} higher than that for $Co(NH_3)_6^{3+}$ and $Rh(NH_3)_6^{3+}$ (Table 4). However, a much larger and more reliable variation is shown by the N–H rocking frequencies. It is suggested that the higher this frequency, the stronger the M–N bond and presumably the weaker the N–H bond.[16]

On this basis data in Table 4 permit an assignment of N–H bond strength in metal hexammines in a decreasing order $Cr^{3+} > Ru^{3+} > Os^{3+} > Co^{3+} > Rh^{3+} > Ir^{3+} > Pt^{4+}$. This clearly does not correlate the rates of hydrogen exchange which decrease in the order $Pt^{4+} > Ru^{3+} > Os^{3+} > Cr^{3+} > Co^{3+} > Rh^{3+} > Ir^{3+}$. That the N–H bond

* The value of 5·7 was checked for $Co(NH_3)_5H_2O^{3+}$ and that of 6·1 for $Ir(NH_3)_5H_2O^{3+}$ obtained by the same method of titration with aqueous alkali.

[12] C. K. JØRGENSEN, *Acta Chem. Scand.* **10**, 500, 518 (1956).
[13] I. KIRSHENBRUM, *Physical Properties of Heavy Water* p. 37. McGraw-Hill, New York (1951).
[14] J. CHATT, L. A. DUNCANSON and L. M. VENANZI, *J. Inorg. Nucl. Chem.* **8**, 67 (1958).
[15] J. N. BRONSTED and K. VOLQVORTZ, *Z. Physik. Chem.* **134**, 97 (1928).
[16] G. F. SVATOS, D. M. SWEENY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 3313 (1957).

strength does not correlate rates of exchange is an indication that N–H bond cleavage is not the only factor involved in exchange and supports the view that crystal field effects are important. Similarly, the rates of exchange do not correlate the nuclear magnetic resonance shifts found for the hexammines of Co^{3+}, Rh^{3+} and Ir^{3+}. JOHNSON[17] finds that the electron shielding of protons decreases in going from $Co(NH_3)_6^{3+}$ to $Ir(NH_3)_6^{3+}$. However it should be mentioned that measurements of proton shielding do not necessarily correspond to acidity.[18]

TABLE 4.—INFRA-RED ABSORPTION SPECTRA OF METAL HEXAMMINES

Complex	NH Stretch	NH Degenerate	NH Symmetric	NH Rock
$[Co(NH_3)_6]Cl_3$	3205	1619 (1620)*	1327 (1325)	828 (827)
$[Rh(NH_3)_6]Cl_3$	3200	1630	1320	825
$[Ir(NH_3)_6]Cl_3$	3220	1640	1350	852
$[Cr(NH_3)_6](NO_3)_3$	3150	1620 (1620)	1310 (1314)	760 (757)
$[Ru(NH_3)_6]Cl_3$	3220	1640	1330	790
$[Os(NH_3)_6]Br_3$	3120	1620	1340	800
$[Pt(NH_3)_6]Cl_4$	3330	1560	1390	942

* Values in parentheses are from ref. 16.

Vol. 15 1960

For the Group VIII elements, the decrease in rate of hydrogen exchange of metal ammines with increasing atomic number of a given triad appears to be fairly general. In addition to the cobalt triad already discussed, data in Table 2 show that the rate of hydrogen exchange of $Ru(NH_3)_6^{3+}$ is one hundred times faster than that of $Os(NH_3)_6^{3+}$, and that of $Pd(en)_2^{2+}$ is ten times faster than $Pt(en)_2^{2+}$. These results can also be explained on the basis of a greater loss of CFSE with increasing atomic number of the metal ion.

(2) *Charge of metal ion.* The effect of the charge of the metal ion on the hydrogen exchange rate of metal ammines should be made by a comparison of isoelectronic systems. Data in Table 2 show that only two such comparisons are possible. Fortunately one is for a pair of octahedral complexes and one for a pair of square complexes. In both cases an increase of one unit charge on the central metal ion results in a very marked increase in acidity and rate of hydrogen exchange of the metal ammine, e.g. $Pt(NH_3)_6^{4+} > Ir(NH_3)_6^{3+}$ and $Au(en)_2^{3+} > Pt(en)_2^{2+}$. Similarly a less direct comparison between a spin-paired d^4 and d^5 system shows $Os(en)_3^{4+} > Os(en)_3^{3+}$. This charge effect cannot be explained on the basis of crystal field stabilization difference as was done above because the largest loss of CFSE should be experienced by Pt(IV). In spite of this, its ammine is the strongest acid suggesting that more important than loss of CFSE is the electrostatic repulsion of the proton by the greater positive charge on the metal. It is further of interest to note that although the charge on the metal ion

[17] R. C. JOHNSON. Private communication.
[18] J. D. ROBERTS, *Nuclear Magnetic Resonance* p. 24. McGraw-Hill, New York (1959).

has a very large effect on the hydrogen exchange rate of metal ammines, the charge on the complex has a small effect.[19] For example $Co(NH_3)_6^{3+}$ exchanges hydrogen only approximately ten times faster than $Co(NH_3)_5\,Cl^{2+}$.

(3) *Electronic configuration of metal ion.* Data in Table 2 permit a comparison of hydrogen exchange rates of octahedral metal ammines of the d^3 type and spin-paired d^5 and d^6 where the metal ions all have a charge of three. Since the rate of exchange decreases with increasing atomic number for any group of elements the comparison should be made between transition metals of the same row. The rate of exchange for the d^3 system $Cr(NH_3)_6^{3+}$ is approximately 1·5 times faster than for the spin-paired d^6 system $Co(NH_3)_6^{3+}$ and the activation energies are 12 and 14 kcal/mole respectively. This difference is in the direction predicted on the basis of the crystal field theory. Thus the d^6 systems suffers a greater loss in CFSE in going from ammine to amido-ammine because of the repulsive interaction between the amido *p*-electrons and the non-bonding *d*-electrons of Co^{3+}. The difference observed is perhaps smaller than expected, since the Cr^{3+} system contains only one electron in each non-bonding *d*-orbital compared to two electrons in each for Co^{3+}. Similarly a spin-paired d^5 system has one *d* orbital containing only one electron so that it is somewhat analagous to d^3, since the repulsive interaction involves only one *d* orbital. However, the experimental results show that $Ru(NH_3)_6^{3+}$ exchanges 3000 times faster than $Rh(NH_3)_6^{3+}$ and $Os(NH_3)_6^{3+}$ is 400 times faster than $Ir(NH_3)_6^{3+}$. The larger difference observed for the second and third row transition metals is consistent with their having a larger crystal field strength than the first row metals. However, the smaller difference between the latter pair is not understood. It may be related to the anomalously large activation energy found for exchange of $Ir(NH_3)_6^{3+}$.

(4) *Co-ordination number.* A comparison can be made between the hydrogen exchange rates of six-co-ordinated and four-co-ordinated metal ammines (Table 2). Unfortunately this comparison is for systems in which the metal ions have different charges and different numbers of *d*-electrons. However to some extent due allowance can be made for the effect of charge and electronic configuration of the metal. Most of the data available are for complexes of Ir^{3+} and Pt^{2+}. The rate of exchange of $Pt(NH_3)_4^{2+}$ is thirty-two times faster than that of $Ir(NH_3)_6^{3+}$ and the activation energies are 11 and 23 kcal/mole respectively. This is not expected on the basis of charge alone but is in accord with the greater loss of CFSE for $Ir(NH_3)_6^{3+}$. There are two other significant differences between these complexes. One is that the $Pt(NH_3)_4^{2+}$ has a vacant p_z orbital. This orbital may possibly hybridize with the d_{zz} orbital in the transition state such that an empty orbital is available to π-bond with the amido electrons resulting in a lower activation energy for exchange. The other difference is that in aqueous solution the Pt^{2+} complex is best represented as $Pt(NH_3)_4(H_2O)_2^{2+}$ having a tetragonal structure with water molecules above and below the $Pt(NH_3)_4^{2+}$ plane. This co-ordinated water might provide a low energy path for hydrogen exchange One possible such path would be to transfer the N–H hydrogen to a co-ordinated oxygen by intramolecular hydrogen bonding and then the rapid exchange of hydrogen from the resulting O–H. This receives some support from the observation[7] that the rates of N–H hydrogen exchange are approximately the same for $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5OH^{2+}$ whereas the latter is expected to exchange more slowly because of its smaller charge.

[19] J. W. Palmer and F. Basolo, *J. Phys. Chem.* In press.

Finally a similar behaviour was observed between $Pd(en)_2^{2+}$ and $Rh(en)_3^{3+}$ for which the relative rates of exchange are seven and one respectively. It should be mentioned that $Pd(en)_2^{2+}$ represents about the limit of lability of metal ammine that can be used to study hydrogen exchange without complication due to M–N cleavage. Thus the value for $Pd(NH_3)_4^{2+}$ is perhaps anomalously high because the hydrogen exchange occurs in part through free ammonia resulting from the ease of dissociation of the ammine complex. This is supported by the observation that the more inert systems $M(en)_2^{2+}$ exchange at relative rates of 10:1 for Pd : Pt whereas ratios of 200 : 1 are obtained for the more labile $M(NH_3)_4^{2+}$ complexes. As a result the choice of metal ammines used in this investigation was limited to inert complexes where the ratio of M–N compared to N–H cleavage is extremely small.

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Vol.
15
1960

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THE PREPARATION OF SODIUM CYANATE BY THE REACTION OF SODIUM METAL WITH UREA*

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Abstract—Sodium cyanate can be prepared in 90 per cent yield and purity by the reaction of sodium dispersions with urea. The reaction may be carried out stepwise, and involves the formation of N-sodio urea which is then decomposed to give sodium cyanate and ammonia.‡

Numerous processes for the preparation of alkali metal cyanates are to be found in the literature. These include the reaction of ammonia and carbon dioxide with alkali metal compounds,[2] the reaction of an alkali metal with urethane,[3] the oxidation of alkali metal cyanides,[4] the reaction of cyanamide with an alkali metal carbonate,[5] and the action of nitrogen on sodium silicate.[6] In commercial practice potassium and sodium cyanates are prepared by allowing urea to react with sodium carbonate.[7] Preparation has also been reported by the reaction of urea with sodium alkoxides.[8]

The latter two methods of preparation probably involve the neutralization of cyanic acid produced by the decomposition of urea with the sodium base,

$$NH_2CONH_2 \xrightarrow{\Delta} HCNO + NH_3\uparrow$$
$$HCNO + Na^+ \rightarrow NaOCN + H^+$$

although a double decomposition reaction

$$NH_4OCN + NaOR \rightarrow NaOCN + ROH + NH_3\uparrow$$

between the sodium base and ammonium cyanate has been proposed.[8] The sodium carbonate route is complicated by the ready formation of sodium cyanurate as a non-separable by-product. This arises from the trimerization of cyanic acid prior to neutralization. The alkoxide process is time consuming because of the slow formation of the alkoxides of higher molecular weight alcohols required for the reaction. Because of these problems we became interested in investigating the reaction between metallic sodium and urea to see if a more attractive process could be developed.

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‡ Process covered by U.S. Patent.[1]

[1] D. O. DePree and E. B. Oldenburg, U.S. Pat. 2729541.
[2] H. T. J. Konig, U.S. Pat. 1971009.
[3] H. Leucho and A. Geserick, *Ber. Dtsch. Chem. Ges.* **41**, 4171 (1908).
[4] P. Pascal, *Traite de Chimie Minerale* Vol. 6, p. 693. Maison et Cie, Paris (1934).
[5] H. T. J. Konig, U.S. Pat. 2208033.
[6] A. R. Lindblad, Brit. Pat. 107426.
[7] A. Scattergood, *Inorganic Synthesis* (Edited by W. C. Fernelius), Vol. 2, p. 88. McGraw-Hill, New York (1946).
[8] R. Bader, D. J. Depre and F. Schutz, *Biochim. Biophys. Acta* **2**, 543 (1948).

Preparation of sodium cyanate by the reaction of urea with both molten bulk sodium and with sodium dispersions was investigated.

The product purities reported are based on analysis of the reaction products for cyanate ion. The amount of urea decomposed is based on ammonia evolution during synthesis. This can only be related to the yield if one assumes that all the ammonia evolved resulted in production of cyanate ion. This of course is not the case, for ammonia is also evolved in the formation of sodium cyanurate.

Equimolar quantities of urea and sodium were employed. Urea reacted slowly with molten sodium at 100–130° with the formation of a product containing 82 per cent sodium cyanate. The yield based on ammonia evolution was 73 per cent. The reaction was complicated by poor wetting of the urea with sodium. This resulted in a large quantity of unreacted sodium which was removed by reaction with alcohol, thus accounting for the discrepancy between the low yield and the reasonably high purity.

A more rapid reaction was obtained when urea was reacted with sodium dispersed in toluene. Particularly interesting was the stepwise nature of this reaction. At approximately 80° hydrogen alone was evolved. On raising the temperature to 100° ammonia began to evolve, and at above 110° the rate of evolution became appreciable. This sequence of reactions indicates that the first reaction to occur is the metalation of urea.

$$2NH_2CONH_2 + 2Na \xrightarrow{80°} 2NaNHCONH_2 + H_2\uparrow$$

Metalation is followed by the decomposition of sodio urea at temperatures over 100°.

$$NaNHCONH_2 \xrightarrow{110°} NaOCN + NH_3\uparrow$$

When the reaction was conducted stepwise in toluene suspension, i.e. maintaining the temperature below 110° for 1 hr and then distilling off the toluene and fusing the sodio compound to complete the decomposition, there was obtained a product of 90 per cent purity in 90 per cent yield. The urea was 98 per cent decomposed as determined by ammonia evolution.

In general it is recommended that, if the latter process is used for preparing sodium cyanate, the product should be used without further purification. Purification of sodium cyanate is carried out by recrystallization from water solution. Because sodium cyanate readily hydrolyses to give ammonia and sodium carbonate, this step can lead to difficulties. Should higher purities be desired, the method of purification reported by Scattergood[7] is recommended.

EXPERIMENTAL

Reaction of urea with molten sodium. Sodium metal (2·3 g, 0·1 mole) was heated to 100–130° in a flask provided with a nitrogen atmosphere, an anchor type stirrer, and a single outlet leading into a flask containing 200 ml of 0·5 N HCl and a single outlet from the latter flask leading to a gas burette. Urea (6 g, 0·1 mole) was added to the molten sodium and the mass was stirred at 100–130° for a period of 2 hr. The reaction mass was then cooled, washed with isopropanol to remove unreacted sodium and urea, dried and analysed for sodium cyanate content. The product analysed 82 wt. per cent sodium cyanate. The urea was 73 per cent decomposed, based on ammonia evolution.

Reaction of urea with dispersed sodium. (A) Urea (12 g, 0·2 mole) was added to heavy aviation alkylate in the equipment described above. The mixture was heated to reflux (approximately 160°) and sodium (4·6 g, 0·2 mole) was added in small pieces. The molten sodium was dispersed by means of high speed stirring. After 30 min the gas evolution essentially ceased. The unreacted sodium was destroyed with isopropanol and the solids were collected by filtration, washed with isopropanol, and

Vol. 15 1960

dried. The product analysed 77 wt. per cent sodium cyanate. The urea was 54 per cent decomposed, based on ammonia evolution.

(B) The above process was repeated using a sodium dispersion in toluene. Urea (12 g, 0·2 mole) was added to 10 g of a dispersion of sodium in toluene containing 4·6 g of sodium (0·2 mole). The mixture was stirred slowly with an anchor type stirrer while being heated. The reaction initiated at 80° as evidenced by the evolution of hydrogen. As the temperature reached 100–110° (after 1 hr heating time) ammonia was evolved slowly but hydrogen continued to be rapidly evolved. The toluene was then distilled off and the reaction mass heated to 165° for another hour to complete the evolution of ammonia. The white product was then cooled and analysed for sodium cyanate content. The product analysed 90 wt. per cent sodium cyanate. The urea was 98 per cent decomposed, based on ammonia evolution. The yield of sodium cyanate was thus 90 per cent.

Analytical method for determination of cyanate ion. The analysis is a modification of the method of LEBOUCQ[9] for cyanate ion and is based on the formation of insoluble hydrazodicarbonamide when inorganic cyanates are reacted with semicarbazide hydrochloride.

$$CNO^- + NH_2CONHNH_2{\cdot}HCl \rightarrow NH_2CONHNHCONH_2 + Cl^-$$

Two changes were made in the LEBOUCQ method which improved its accuracy and precision. Semicarbazide hydrochloride was added as a solution instead of the solid reagent. This eliminated precipitation on the crystals and ensured complete reaction. Secondly, a 1 ml excess of acetic acid was added in those cases where the solution was basic after addition of the semicarbazide hydrochloride.

An analysis is conducted by adding a weighed sample of the unknown to an aqueous solution of semicarbazide hydrochloride and acidifying with acetic acid. This mixture is stirred, allowed to stand 24 hr, and filtered. The precipitate is washed with a saturated solution of hydrazodicarbonamide, dried at 110° and weighed.

Cyanide, carbonate, biuret, urethane and urea, which may be present in preparations of cyanates, do not interfere.

[9] M. J. LEBOUCQ, *J. Pharm. Chim.* **5**, 531 (1927).

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POTASSIUM NITRITE: PREPARATION AND THERMOMETRIC ANALYSIS*

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Abstract—Commercial potassium nitrite which always contains several per cent potassium nitrate cannot be purified by recrystallization. Sodium nitrite can be so purified, and was used to prepare the nitrite form of an anion exchange resin. The nitrite resin was used to remove the nitrate content of "Reagent Grade" commercial potassium nitrite.

It was found that the temperature of the first order phase transition of potassium nitrite at 39·14° is raised by the presence of potassium nitrate and lowered by potassium chloride. This temperature change was used as a sensitive indication of the amount of either impurity.

REAGENT grade and C.P. potassium nitrite samples which are commercially available contain 5–10 per cent potassium nitrate impurity. It is impossible to decrease the nitrate content effectively by fractional crystallization. BUREAU[1] has shown that a solid solution of potassium nitrate in potassium nitrite forms as a precipitate in equilibrium with an aqueous phase having practically the same ratio of nitrate to nitrite. A similar lack of separability was found by SLAVINA[2] for the system potassium chloride, potassium nitrite. However, pure sodium nitrite can be fractionally crystallized from impurities contained in the commercial material, and indeed, 99·9 per cent sodium nitrite is commercially available. Thus by use of an anion exchange resin, the nitrate impurity of potassium nitrite can be transferred to sodium nitrite from which the nitrate can be removed by fractional crystallization.

The literature pertaining to potassium nitrite is filled with reports of experiments made with "pure" potassium nitrite. Much of this data is useless due to the highly impure state of the material. The present article is an attempt to present an easy method for preparation of a realistic Reagent Grade potassium nitrite the economy of which is hoped will result in an improved commercial material.

EXPERIMENTAL

Materials

Commercial sodium nitrite containing about 3 per cent sodium nitrate as the only significant impurity was subjected to recrystallization by the "double withdrawal" scheme described by TIPSON[3]. The relevance of this purification method is substantiated by existing data for the system $NaNO_2$–H_2O containing the following third components: sodium nitrate,[1,4] sodium chloride,[4] sodium carbonate,[1] sodium bicarbonate,[1] and potassium nitrite.[5] Pure sodium nitrite is reported to have been

* This research was carried out in part at the School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.

[1] J. BUREAU, *Ann. Chim.* (11*th Ser*) **8**, 5 (1937).
[2] D. S. SLAVINA, *Chem. Zentralblatt* **2**, 1546 (1931).
[3] R. S. TIPSON, Chapter 3 in *Techniques of Organic Chemistry* (2nd Ed., Edited by A. WEISSBERGER) Vol. 3, Part I, Chap. 3. Interscience, New York (1956).
[4] A. V. RAKOVSKII and D. S. SLAVINA, *Trans. Inst. Pure Chem. Reagents* (Moscow), No. 11, 20 (1931); *Chem. Abstr.* **26**, 2369 (1932).
[5] N. K. VOSKRESENSKAYA and S. I. BERUL, *Izv. Sektora Fiz.-Khim. Anal., Inst. Obsch. Neorg. Khim., Akad. Nauk SSSR* **25**, 314 (1954).

Vol. 15 1960

prepared by fractional crystallization of commercial sodium nitrite by SLAVINA,[5] and by DIVERS.[6] BUREAU's[1] data indicates that it is necessary to remove bicarbonate from the nitrite before recrystallization.

Amberlite IRA-400—50 to 100 mesh anion exchange resin was used in the nitrite form after exhaustively replacing its chloride anions with nitrite by passing through a solution of sodium nitrite which was purified as above.

Reagent Grade commercial potassium nitrite containing 4–7 per cent potassium nitrate as the only significant impurity was used. The nitrate impurity was not mentioned on the labels of the various commercial products available.

Apparatus and method

Five pounds of the anion exchange resin was contained in a Pyrex tube 40 mm i.d. by 1·2 m long tapered to an outlet at the bottom. A small plug of glass-wool was used to hold the resin in place at the bottom of the column. A layer of glass-wool held in place by a layer of glass beads prevented disturbance of the resin at the top of the column.

Placing the resin in the Pyrex tube so as to insure a uniform bed which is free from channelling was found to be a highly critical operation. The method used has not been previously described. The resin was suspended in a solution of sodium nitrite which was adjusted to have very nearly the same density as the resin. The suspended material was then poured into the column. After the excess solution had been drained out the bottom and the column had been washed, the bed was always found to operate with a maximum exchange capacity.

Pure potassium nitrite was prepared by passing "Reagent Grade" potassium nitrite through the nitrite form of the anion exchange resin. This procedure served to eliminate the nitrate impurity in the potassium nitrite. Operation of the column was found to confirm the equilibrium constants given for the commercially equivalent resin Dowex 2 by WHEATON and BAUMAN[7]. One molar solutions were used in both exchange and regeneration of the resin. The nitrate content of the effluent potassium nitrite from the column was followed by running cooling curves on successive evaporated 1 l. portions as described below.

There was no loss of capacity of the column after 100 cycles.

THERMOMETRIC ANALYSIS OF POTASSIUM NITRITE

Since all common impurities except chloride and nitrate can be removed from potassium nitrite by fractional recrystallization, a rapid method of analysis unique to these impurities is desirable.

It was found that the pure potassium nitrite prepared by the above method has a first order transition at 39·14 ± 0·02°. This transition temperature was obtained with a thermometer which had graduations of 0·1°. The thermometer had been calibrated against a U.S. Bureau of Standards thermometer. Potassium nitrite prepared by the reaction of silver nitrite with potassium chloride in a dilute 0·1 molar solution had the same transition temperature. Analysis of both of these samples for nitrite by permanganate titration as well as conversion to the chloride confirmed that the samples were at least 99·9% KNO_2. The temperature of this transition is raised by the presence of potassium nitrate and is lowered by the presence of potassium chloride. Cooling curves were all run on samples which had been evaporated just to saturation at the boiling point and 760 mm Hg. The reason for not taking the samples to dryness is that successive recrystallization of potassium nitrite containing small amounts of either nitrate or chloride has no effect on the composition of the solid phase. Therefore, there is no point in drying the material. Further, the wet material gives a much sharper break in the cooling curve. Between 0 and 5 per cent potassium nitrate, there is a linear increase in transition temperature with increase in nitrate content of 0·48° for

[6] E. DIVERS, *J. Chem. Soc.* **75**, 85 (1899).
[7] R. M. WHEATON and W. C. BAUMAN, *Industr. Engng. Chem.* **43**, 1088 (1951).

each 1·00 per cent potassium nitrate content. Ten per cent potassium nitrate raises the transition temperature 5·5°. The transition temperature of potassium nitrite containing 0·50 per cent potassium chloride is lowered 5·1°. In practice, no significant amount of chloride was found in any of the diverse commercial potassium nitrite samples that were used. However, when present, chloride may be removed easily by titration with silver nitrite. Consideration of the equilibrium constant for formation of the silver nitrito complex at room temperature given by CAVALCA *et al.*[8] indicates that such titration should be done with a solution at least as dilute as 0·1 molar in nitrite.

It should be noted that chemical analysis of the potassium nitrite samples was effected by permanganate titration. It should be appreciated that nitrate content of nitrites is based on the total nitrite content. Small amounts of nitrate cannot be chemically detected independently of the nitrite. Thus, the transition temperature reported above, 39·14° represents a new criteria of purity. Justification of the claim of purity is based on knowledge of the physical chemistry of the phase systems relevant to removal of the possible impurities of the sodium nitrite starting material and the physical chemistry of the ion exchange resin. The theory of ion-exchange resins as related to product purity has been adequately discussed by WINTER[9].

Acknowledgement—The author wishes to express his appreciation for the many illuminating discussions with Professor S. WINTER on the applicability of ion-exchange methods to the solution of this problem.

[8] L. CAVALCA, M. NARDELLI and A. BRAIBANTI, *Gazz. Chim. Ital.* **83**, 476 (1953).
[9] S. S. WINTER, *J. Chem. Educ.* **33**, 246, 473 (1956).

Vol. 15 1960

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THE HYDROGEN–VANADIUM(V) OXYTRICHLORIDE REACTION*

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Abstract—The reaction of hydrogen and $VOCl_3$ has been investigated over the temperature range 500–850°C. Pure VOCl was obtained as the reaction product at 600–635°C; but at higher temperatures mixtures of V_2O_3, VCl_2 and VOCl resulted. Thermal decomposition of VOCl at 650–900°C proceeded with the formation of V_2O_3, VCl_2, VCl_3 and VCl_4; this reaction was related in a definite way to the hydrogen reduction. X-ray powder diffraction data are given for VOCl and VCl_2.

Since the original work of Roscoe[1] little additional information has appeared in the literature concerning the reduction of vanadium(V) oxytrichloride with hydrogen. Among the products obtained in this reaction were VOCl and V_2O_3, but detailed reaction conditions were not given. Ruff and Lickfett[2] described the preparation of vanadium(III) oxychloride by the partial decomposition of vanadium(III) chloride in a stream of carbon dioxide. This method, however, leaves much to be desired since the starting material is relatively difficult to prepare. By comparison, the hydrogen reduction of vanadium(V) oxytrichloride would be a much more convenient preparation providing the reaction proceeds cleanly. For this reason a more detailed investigation of this reaction was undertaken.

EXPERIMENTAL

Reaction of $VOCl_3$ *and hydrogen*

The vanadium(V) oxytrichloride used in this investigation was prepared by the reaction of chlorine with a mixture of carbon and vanadium pentoxide in a molar ratio 3:2 at 350–450°C. Subsequent to use, the liquid was distilled through a 25 mm o.d. column packed to a height of 18 in. with glass helices; only the middle fraction boiling at 126·5°C was retained for use in this study.

The reactions were performed with electrolytic grade hydrogen which was purified by passing the gas successively through a "Deoxo" catalytic oxygen remover, a sulphuric acid scrubber, and finally a trap maintained at −190°C to remove the last traces of moisture. Thence, the gas was bubbled through the liquid vanadium(V) oxytrichloride, the vapour-pressure of which was adjusted by means of an appropriate temperature bath. For most of the reactions this temperature was not closely controlled and corresponded to the room temperature, i.e. ca. 22°C.

The reaction chamber consisted of a 2·5 cm o.d. × 30 cm long, Vycor tube which was heated by means of a manually controlled resistance furnace. Before entering the reaction tube the gaseous mixture was preheated to 400°C in a tube of similar dimensions. Gaseous products were conducted to the hood through a sulphuric acid scrubber, which served to protect the system from the atmosphere.

The products of the reaction were identified by analysis and X-ray powder diffraction patterns. Manipulation and transfer of all solid products was carried out in a glove box under a dry, helium atmosphere.

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] H. E. Roscoe, *J. Chem. Soc.* **21**, 342 (1868).
[2] O. Ruff and H. Lickfett, *Ber. Dtsch. Chem. Ges.* **44**, 506 (1911).

Thermal decomposition of VOCl

Samples of VOCl prepared by the hydrogen reduction of $VOCl_3$ were transferred to a Vycor tube in the dry-box and the tube was then connected to the vacuum rack through a stopcock and ball-joint. After evacuation of the tube to a pressure of less than 10^{-3} mm, the sample was heated slowly by means of a resistance furnace to temperatures in the range 600–900°C. Volatile components evolved during decomposition were condensed in a trap maintained at −190°C. The products were identified by analysis and X-ray powder diffraction patterns.

RESULTS AND DISCUSSION

The reduction reactions were performed at temperatures in the range 550 to 850°C. In all cases a large excess of hydrogen was utilized; the hydrogen pressure was essentially 1 atm while that of the $VOCl_3$ was maintained in the range 20-100 mm. The reaction products obtained at the various temperatures are given in Table 1.

Table 1.—Products of the $VOCl_3$–H_2 reaction at various temperatures

Temperature (°C)	Relative amounts of products			
	V_2O_3	VCl_2	VOCl	V
550	—	—	trace	—
600	—	—	major	—
610	—	—	major	—
635	—	—	major	—
650	trace	trace	major	—
690	moderate	moderate	moderate	—
700	moderate	moderate	moderate	—
755	major	trace	—	—
850	major	—	—	present

At temperatures less than 600°C only very small quantities of VOCl were obtained even though the reaction was continued over long periods of time. As indicated in Table 1, a mixture of products resulted for temperatures exceeding ca. 635°C. Thus the useful temperature range for preparation of VOCl by this reaction is limited on the lower end by the slow reaction rate and on the upper end by the occurrence of competitive reactions. Within this narrow temperature range, the VOCl was obtained as large, shiny brown flakes of good purity (Found: V, 49·9; Cl, 34·2. Calc. for VOCl: V, 49·8; Cl, 34·6%)

For temperatures in excess of 650°C but less than 750°C, a mixture of V_2O_3, VCl_2 and VOCl resulted from the reaction. All lines obtained from powder diffraction patterns of these mixtures could be accounted for by comparison with the corresponding patterns given by the pure substances. In the case of those reactions performed at temperatures over 750°C, the product consisted of a mixture of V_2O_3 and vanadium metal. Only one *d*-spacing corresponding to that of vanadium metal could be found in the powder patterns of these mixtures. This observation, however, is not surprising since all but two of the lines for the metal are of relative intensity less than five. Thus, the less intense lines for vanadium are difficult to observe in a mixture where the metal is the minor component.

Since the only product of the hydrogen reduction was VOCl at the lower temperatures, it seemed probable that VOCl was also the initial product at the higher temperatures. However, in the latter case, a mixture could be obtained as a result of further

Vol. 15 1960

reaction of VOCl with hydrogen or by thermal decomposition of the VOCl. Consequently, the thermal stability of VOCl at elevated temperatures was investigated. At a pressure of ca. 10^{-3} mm, 650°C was the lowest temperature at which decomposition was evident. At higher temperatures the reaction was more rapid, but in each case up to 900°C the products were the same. A non-volatile residue of V_2O_3 and VCl_2 was produced, while a band of VCl_3 sublimed to the cool zone of the furnace tube. The more volatile VCl_4 was obtained as a brown solid in the liquid nitrogen trap.

TABLE 2.—PRINCIPAL X-RAY DIFFRACTION LINES FOR VOCl AND VCl_3

VOCl				VCl_3			
hkl	*d* (Å) Calc.	*d* (Å) Obs.	I/I_1	*hkl*	*d* (Å) Calc.	*d* (Å) Obs.	I/I_1
001	7·97	7·97	100	003	5·83	5·83	100
101	3·42	3·42	100	010	3·07	3·08	10
012	2·54	2·54	100	006	2·92	2·92	2
111	2·38	2·37	70	103	2·75	2·74	30
013	2·07	2·06	50	104	2·54	2·54	30
200	1·89	1·89	50	106	2·13	2·13	5
113	1·82	1·82	80	107	1·95	1·95	1
020	1·65	1·65	10	110	1·80	1·80	95
212	1·52	1·52	70	113	1·72	1·72	40
121	1·49	1·49	20	024	1·47	1·46	15
221	1·23	1·24	20	214	1·13	1·13	15
				300	1·04	1·04	5

From a consideration of the products obtained, the following equations can be written to explain the thermal decomposition of VOCl:

$$3VOCl = V_2O_3 + VCl_3 \quad (1)$$

$$2VCl_3 = VCl_2 + VCl_4 \quad (2)$$

or

$$6VOCl = 2V_2O_3 + VCl_2 + VCl_4. \quad (3)$$

Reactions (1) and (3) probably occur simultaneously, although at the higher temperature reaction (3) should become relatively more important. This must be the case since VCl_3 becomes increasingly unstable with respect to decomposition via reaction (2) with increasing temperature.[2] Especially noteworthy is the observation that the first noticeable decomposition of VOCl occurred at 650°C, which is the temperature at which mixtures were first evident in the hydrogen–$VOCl_3$ reaction.

A plausible explanation of the products obtained in the hydrogen reduction is given by the reactions,

$$VOCl_3 + H_2 = VOCl + 2HCl \quad (4)$$

$$2VCl_3 + H_2 = 2VCl_2 + 2HCl \quad (5)$$

$$VCl_4 + H_2 = VCl_2 + 2HCl \quad (6)$$

$$VCl_2 + H_2 = V + 2HCl \quad (7)$$

in addition to reactions (1), (2) and (3). In the presence of hydrogen at 650°C or more, VCl_2 is the only halide observed, since both VCl_3 and VCl_4 are readily reduced under these conditions. At ca. 700°C reaction (7) becomes important;[3] thus, the products obtained in this temperature region should be V_2O_3 and vanadium metal, as observed.

In the course of this work the crystal structures of VOCl and VCl_2 were determined from their powder diffraction patterns. VOCl is orthorhombic with $a_0 = 3{\cdot}78$ Å, $b_0 = 3{\cdot}30$ Å and $c_0 = 7{\cdot}97$ Å; it is isostructural with TiOCl.[4] The VCl_2 was found to be rhombohedral with $a_0 = 6{\cdot}20$ Å and $\alpha = 33{\cdot}8°$; the structure may also be represented by a pseudo-hexagonal cell with $a_0' = 3{\cdot}60$ Å and $c = 17{\cdot}50$ Å. The principle lines for these substances are given in Table 2. The X-ray data for VCl_2 was obtained with material that had been sublimed from the V_2O_3–VCl_2 mixtures at 900°C and ca. 10^{-3} mm.

[3] G. Jantsch and F. Zemek, *Monatsh.* **84**, 1119 (1953).
[4] H. Schäfer, F. Wartenpful and E. Weise, *Z. Anorg. Chem.* **295**, 268 (1958).

Vol. 15 1960

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THE DENSITY OF MOLTEN METAL FLUORIDES IN THE RANGE OF 1600°–2500°K

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Abstract—Using a graphite crucible and a tungsten sinker, the liquid densities of the alkaline-earth and two rare-earth fluorides were determined by the immersed-sinker method, over the temperature range of 1600°–2500°K. The molar volumes and thermal coefficients of expansion were calculated from the liquid densities and were correlated with those of the alkali-metal fluorides. The liquid-molar volumes of the alkaline-earth fluorides exhibit a linear relationship when plotted against the period in the Periodic Table.

A BASIC knowledge of the physical properties of materials at high temperatures is becoming of increasing importance. A check of the literature on molten fluorides as well as on oxides and other salts, showed that very few data are available above 1500°K. The only data reported for a temperature range above this temperature are those published in the Soviet Union by MASHOVETZ and LUNDINA[1]. These workers measured the density of molten calcium fluoride up to 1700°K, using a platinum crucible. Data available above 1700°K were determined only for salts and oxides at their melting points by means of the drop method.[2–5] The only density measurements reported on pure molten fluorides besides those by MASHOVETZ and LUNDINA were those made by JAEGER[6] in 1917, who determined the liquid density of the alkali-metal fluorides from 1100° to 1770°K.

The scarcity of data is mainly due to the lack of materials suitable at elevated temperatures. These materials must withstand the high temperatures as well as resist reaction with the fluorides. Platinum and iridium, which are normally used, are not utilizable due to their low melting and softening points. After some study as to what material will not react with the fluorides above 1700°K, it was found that tungsten could be used as a sinker with the fluorides to be studied. This metal was not used as the crucible material due to the high cost of fabrication. Further study showed that graphite does not react with the six fluorides reported in this paper and it was therefore used.

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† This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF18(600)-1475.

[1] V. P. MASHOVETZ and Z. F. LUNDINA, *Ukrain. Akad. Nauk Inst., Proc. First All Union Conf. on Aqueous Solutions* pp. 191–212 (1935).
[2] H. V. VARTENBERG, G. WEHNER and E. SARAN, *Nachr. Ges. Wiss. Gottingen, Math.-Physik Klasse, Fachgruppe* II, (N.F.) **2**, 73 (1936).
[3] A. W. PETERSON, H. KEDESDY, P. H. KECK and E. SCHWARZ, *J. Appl. Phys.* **29**, 213 (1958).
[4] A. CALVERLEY, *Proc. Phys. Soc.* B **70**, 1040 (1957).
[5] W. D. KINGERY, *J. Amer. Ceramic Soc.* **42**, 6 (1959).
[6] F. M. JAEGER, *Z. Anorg. Chem.* **101**, 1 (1917).

EXPERIMENTAL

Apparatus

In these studies, the source of heat was a carbon-tube resistance furnace operating in an argon atmosphere. The furnace consisted of (G) a 3 in. carbon tube (grade GA National Carbon pipe, 97 per cent carbon) with (D) copper electrodes on each end. The tube was centred in the metal shell and insulated with (H) Thermax carbon black. The furnace lids (E and N) were made of transite. Argon (A) was fed into the furnace through the metal shell and at the bottom through the transite lid (N).

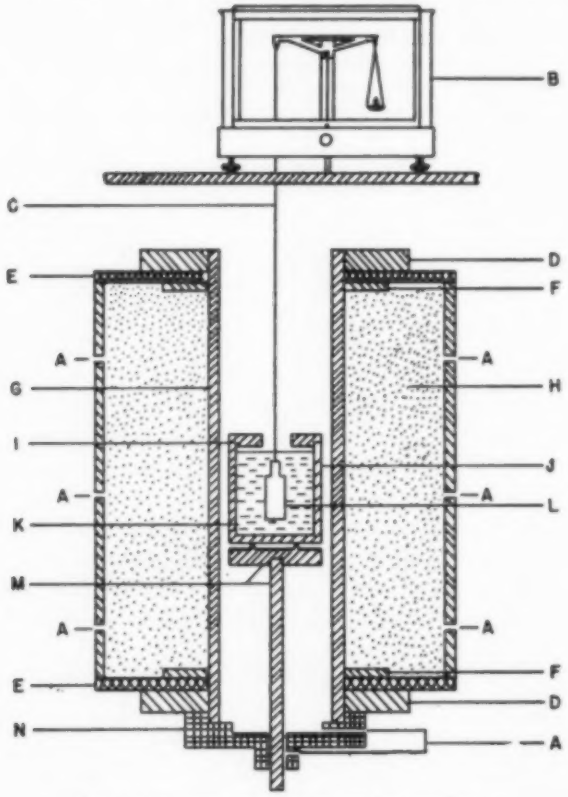

FIG. 1.—Density apparatus for molten fluorides.

When measuring the density of the liquid fluorides, a graphite crucible (J) 2 in. o.d. and 3 in. high was used. The crucible was made from grade E-821 Dixon graphite and had a purity of 99·8 + per cent carbon. The crucible containing the melt (K) was supported in the centre of the furnace on a graphite platform (M) of the same purity, as is shown in Fig. 1. A pure-tungsten rod $\frac{1}{8}$ in. in diameter and $1\frac{1}{4}$ in. high was used as a sinker (L). The sinker was suspended from the analytical balance (B) by means of a tungsten wire (C).

Procedure

The densities of the liquid fluorides were determined by the suspended-sinker method. The procedure consisted in measuring the loss of weight of the sinker in the molten fluoride while determining the furnace temperature simultaneously by means of a calibrated optical pyrometer (melting points of nickel, platinum and iridium). The reproducibility of the pyrometer readings was ±15°K. By taking numerous readings, however, the final temperature values had a probable error of 2°K or 0·08 per cent. The readings were made by sighting the pyrometer on the graphite crucible, just at the surface of the melt and were corrected for the emissivity of the graphite.

Vol. 15 1960

The volume of the tungsten sinker was always corrected to the operating temperature, V_T, using the thermal coefficient of expansion data reported by WORTHING[7]. The density of the tungsten used was 19·222 g/cm³ at 298·5°K (25.3°C). The density of the melt was calculated from the equation

$$D = \frac{W_A - W_M}{V_T},$$

where W_A and W_M are the weights of the sinker in air and in the melt, respectively. The value obtained from the above equation was always corrected for the buoyancy in air. This correction was, for example, +0·0005 g/cm³ for liquid strontium fluoride.

After each density run the melt was analysed for total carbon, oxide and carbide. The maximum impurities found were 0·1 per cent carbon, 0·1 per cent carbide and 0·15 per cent oxide. If these were neglected, the density of CaF_2 would have been low by 0·0017 g/cm³ (0·07 per cent error). Similar results were found for the other fluorides.

Compounds used

The fluorides used in these studies were all predried by heating slowly first to 100°C and finally to 300°C while evacuating to less than 1 mm of Hg. This procedure was followed in order to prevent the reaction of the fluoride with water at high temperatures with the formation of the oxide and HF. The fluorides used and their purities were as follows:

Fluoride	Source	Purity (%)
CaF_2	J. T. Baker Analysed	99·96
BaF_2	Baker & Adamson Reagent Grade	99·6
SrF_2	Baker & Adamson Reagent Grade	99·9
MgF_2	Baker & Adamson Purified, dried	99·0
LaF_3	Lindsay Chemical	99·99
CeF_3	Lindsay Chemical	99·9

RESULTS

Using the above method, the liquid densities of the Group IIA fluorides (calcium fluoride, magnesium fluoride, strontium fluoride and barium fluoride) as well as the two lanthanide fluorides (lanthanum fluoride and cerous fluoride) were determined. The data obtained[8] are shown in Figs. 2 and 3. The data fall on straight lines when plotted against temperature. The equations of these lines are given in Table 1.

Using the smoothed-density values obtained from the above density equations, the molar volumes for the liquid fluorides were calculated and are summarized in Tables 2 and 3.

TABLE 1.—DENSITY OF MOLTEN FLUORIDES

Fluoride	Temperature (°K)	Density equation
MgF_2	1650–2100	$D = 3{\cdot}235 - 5{\cdot}24 \times 10^{-4}T$
CaF_2	1640–2300	$D = 3{\cdot}179 - 3{\cdot}91 \times 10^{-4}T$
SrF_2	1750–2200	$D = 4{\cdot}784 - 7{\cdot}51 \times 10^{-4}T$
BaF_2	1600–2000	$D = 5{\cdot}775 - 9{\cdot}99 \times 10^{-4}T$
LaF_3	1750–2450	$D = 5{\cdot}793 - 6{\cdot}82 \times 10^{-4}T$
CeF_3	1700–2200	$D = 6{\cdot}253 - 9{\cdot}36 \times 10^{-4}T$

[7] A. G. WORTHING, *Phys. Rev.* **10**, 638 (1917).
[8] A. D. KIRSHENBAUM and J. A. CAHILL, *Technical Note No.* 9. Research Institute, Temple University, (1959); Air Force Office of Scientific Research Technical Document No. 59–844.

When the liquid-molar volumes of the Group IIA fluorides are plotted against the ratio of temperature to boiling point in degrees Kelvin, $T/T_{b.p.}$,* a family of straight lines is obtained. A comparison of the molar volumes of these fluorides in the solid state at 295°K and in the liquid state, when $T/T_{b.p.}$ equals 0·75, is shown in Fig. 4, where the molar volumes are plotted according to their period in the Periodic Table.

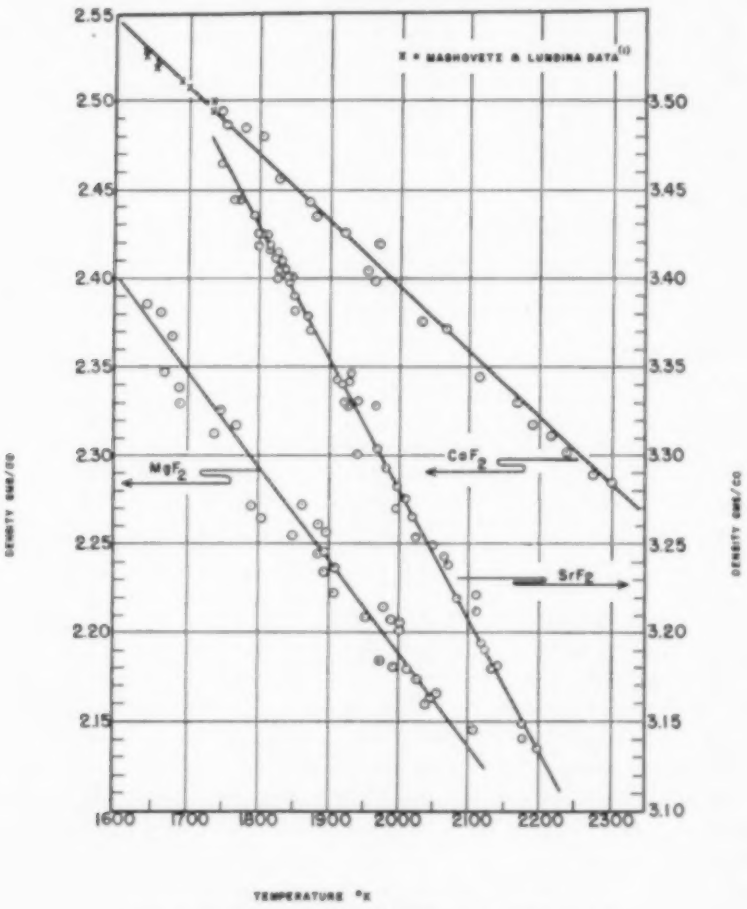

FIG. 2.—Density of molten fluorides (MgF_2, CaF_2, SrF_2).

It is interesting to note that the solid and liquid molar volumes fall on almost similar curves, the liquid-molar volumes falling on a nearly straight line. The same phenomenon is observed upon correlating the literature data on the alkali-metal fluorides (Group IA fluorides) reported by JAEGER[6] and ZACHARIASIN[12].

The relationship between volume, V, and cubical coefficient of expansion, β, is

$$V_t = V_t(1 + \beta t).$$

* $T/T_{b.p.}$ was used instead of T/T_C because the critical temperature of most of these fluorides are not known.

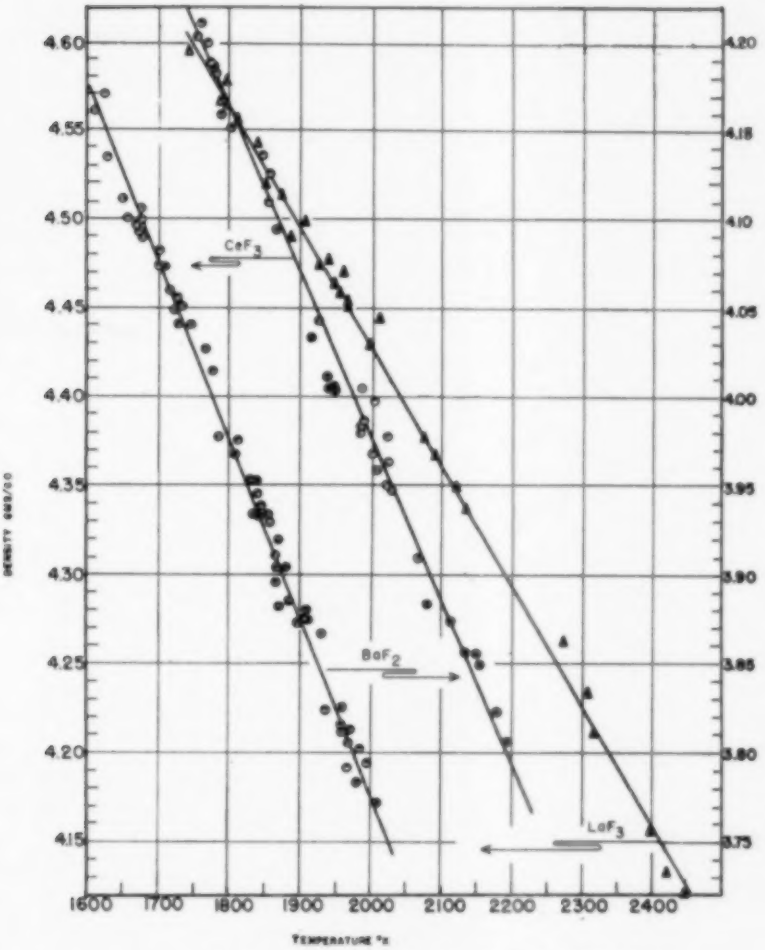

FIG. 3.—Density of molten fluorides (BaF_2, LaF_3, CeF_3).

where i and t are initial and final temperatures. For a given weight of melt the equation becomes

$$\frac{1}{D_t} = \frac{1}{D_i}(1 + \beta t)$$

$$D_i = D_t(1 + \beta t)$$

$$\frac{dD}{dt} = \beta D_t.$$

where D is the density of the melt.

Using the above equation, the cubical coefficients of expansion for the molten fluorides were calculated for various temperatures and are tabulated in Table 4. A comparison of the coefficient of expansion of liquid and solid calcium fluoride over

TABLE 2.—LIQUID MOLAR VOLUMES OF GROUP II A FLUORIDES

Temp. (°K)	MgF_2			CaF_2			SrF_2			BaF_2		
	$T/T_{b.p.}$*	Density (g/cm³)	Molar volume (cm³/mole)	$T/T_{b.p.}$*	Density (g/cm³)	Molar volume (cm³/mole)	$T/T_{b.p.}$*	Density (g/cm³)	Molar volume (cm³/mole)	$T/T_{b.p.}$*	Density (g/cm³)	Molar volume (cm³/mole)
1600	—	—	—	—	—	—	—	—	—	0·643	4·177	41·99
1700	0·680	2·345	26·58	0·612	2·514	31·06	—	—	—	0·683	4·077	43·02
1800	0·720	2·292	27·19	0·647	2·475	31·55	0·654	3·433	36·60	0·723	3·977	44·10
1900	0·760	2·240	27·82	0·683	2·436	32·06	0·691	3·358	37·41	0·763	3·877	45·23
2000	0·800	2·187	28·49	0·719	2·396	32·58	0·727	3·283	38·27	0·803	3·777	46·43
2100	0·840	2·137	29·19	0·755	2·357	33·12	0·764	3·208	39·17	—	—	—
2200	—	—	—	0·791	2·318	33·68	0·800	3·133	40·11	—	—	—
2300	—	—	—	0·827	2·279	34·26	—	—	—	—	—	—
solid	—	—	20·14[9]	—	—	24·55[10]	—	—	29·8[11]	—	—	35·65[8]

* $T/T_{b.p.}$ = temperature/boiling point in °K.

[9] Calculated from X-ray data compiled by JOHN G. ALBRIGHT. *Handbook of Chemistry and Physics* (38th Ed.) pp. 2448–2462 (1956–1957).
[10] B. W. ANDERSON and C. J. PAYNE, *Gemnologist* **9**, 119 (1940); GMELIN, *Handbuch der Anorganischen Chemie*, System No. 28. Part B, Sec. 2, p. 403 (1957).
[11] W. BILTZ, *Z. Anorg. Chem.* **115**, 241 (1921).
[12] W. F. ZACHARIASEN, *Z. Krist.* **80**, 137 (1931) (from X-ray data).

Vol. 15 1960

the whole range of present knowledge; i.e from 0° to 2300°K is shown in Fig. 5. At the melting point the linear coefficient of expansion, α, of the solid (extrapolated) is $31{\cdot}7 \times 10^{-6}$, while that for the liquid is $54{\cdot}7 \times 10^{-6}$. These values correspond to a volume increase, $\Delta V/V_{solid}$, of 11·5 per cent upon melting.

TABLE 3.—MOLAR VOLUMES OF LIQUID LaF_3 AND CeF_3

Temp. (°K)	$T/T_{b.p.}$	LaF_3		CeF_3	
		Density g/cm³	Molar volume (cm³/mole)	Density (g/cm³)	Molar volume (cm³/mole)
1700	0·654	—	—	4·662	42·29
1800	0·692	4·565	42·92	4·568	43·15
1900	0·731	4·497	43·57	4·475	44·05
2000	0·769	4·429	44·24	4·381	45·00
2100	0·808	4·360	44·93	4·288	45·98
2200	0·846	4·292	45·65	4·194	47·00
2300	0·885	4·224	46·38	—	—
2400	0·923	4·156	47·14	—	—
295	(solid)	5·996	32·67[9]	6·164[9]	31·98

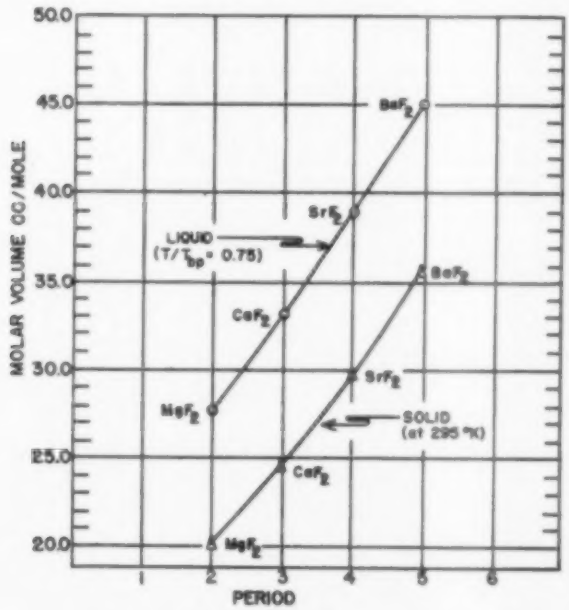

FIG. 4.—Period vs. molar volume group IIA fluorides.

DISCUSSION OF RESULTS

A comparison of the molar volumes shows that the molar volumes of the liquid fluorides in Periods 3, 4 and 5 are the same whether or not they are in Groups IA, IIA or IIIA. For example, the molar volumes of liquid KF and CaF_2 are 33·02 and 33·07,

TABLE 4.—CUBICAL THERMAL COEFFICIENT OF EXPANSION OF MOLTEN FLUORIDES

Temperature (°K)	MgF_2 $\beta \times 10^4$	CaF_2 $\beta \times 10^4$	SrF_2 $\beta \times 10^4$	BaF_2 $\beta \times 10^4$	LaF_3 $\beta \times 10^4$	CeF_3 $\beta \times 10^4$
1600	—	—	—	239·1	—	—
1700	223·4	155·7	—	245·0	—	200·8
1800	228·5	158·2	218·7	251·2	149·4	204·9
1900	233·9	160·7	223·6	257·6	151·7	209·2
2000	239·5	163·3	228·7	264·4	154·0	213·6
2100	245·3	166·0	234·1	—	156·4	218·3
2200	—	168·8	239·7	—	158·9	223·2
2300	—	171·8	—	—	161·5	—
2400	—	—	—	—	164·1	—

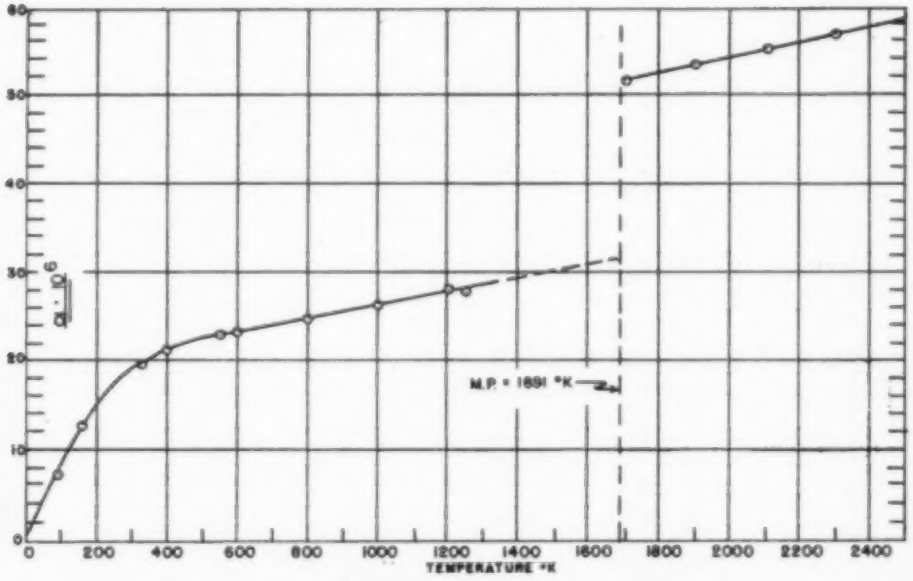

FIG. 5.—Linear coefficient of expansion of CaF_2 from 0°K to 2500°K.

of RbF and SrF_2, 38·75 and 38·88 and of CsF, BaF_2, LaF_3 and CeF_3, 44·84, 44·95, 44·00 and 44·65, respectively. If liquid-molar volumes of 33·0 and 38·8 are assumed for ScF_3 and YF_3 at $T/T_{b.p.} = 0{\cdot}75$, the density of ScF_3 at 1350°K would be 3·09 g/cm³ and of YF_3 at 1875°K, 3·76 g/cm³.

Fig. 4 shows that an almost straight-line relationship exists when the liquid-molar volumes of the Group IIA fluorides at $T/T_{b.p.} = 0{\cdot}75$ are plotted according to their period in the Periodic Table. An extrapolation of the data shows that molar volume of liquid radium fluoride at 1650°K would be 51 cm³/mole, which corresponds to a density of 5·18 g/cm³.

Acknowledgements—The authors wish to thank Dr. A. V. GROSSE for his helpful suggestions and Mrs. LUCIA STRENG for making the density measurements of solid CaF_2 and for determining the impurities in the melts.

Vol. 15 1960

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THERMAL DECOMPOSITION OF NITROGEN-15 LABELLED HYDRAZINE

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(*Received* 18 *December* 1959)

Abstract—The thermal decomposition of gaseous hydrazine is at least in part heterogeneous. In a quartz or glass vessel the reaction proceeds according to the equation $3N_2H_4 \rightarrow 4NH_3 + N_2$.

A study of the isotopic composition of molecular nitrogen from the thermal decomposition of hydrazine enriched in $H_2{}^{15}N\text{–}{}^{14}NH_2$ between 270°C and 325°C shows that no randomization of the nitrogen atoms occurs during the reaction. Lack of randomization clearly signifies that the N–N bond existing in molecular nitrogen has not broken during the process of decomposition. Reaction mechanisms are discussed in the light of this result. It is shown that free radical paths involving homogeneous gaseous reactions are probably not operative. The proposal by SZWARC[3] that the decomposition of hydrazine occurs through a surface adsorbed activated complex is consistent with the results of the randomization studies.

THE thermal decomposition of gaseous hydrazine has been studied previously[1,2,3] and has been shown to be at least in part heterogeneous. In a quartz or Pyrex vessel the reaction occurs according to the equation

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{1}$$

although small amounts of hydrogen are also formed. The reaction according to our experiments and others[1,2,3] is approximately first order and between 250°C–350°C the mole ratio of the hydrogen formed to nitrogen formed varies between 0·05 to 0·10.

The possible mechanisms of decomposition are limited to a large extent by the stoicheiometry of equation (1). Perhaps the simplest reaction path consistent with both the stoicheiometry of equation (1) and the first order kinetics is

$$N_2H_4 \text{ (surface)} \rightarrow 2NH_2 \tag{2}$$

$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \tag{3}$$

$$2N_2H_3 \rightarrow 2NH_3 + N_2 \tag{4}$$

where equation (2) represents a surface reaction and is the rate determining step. Reactions (3) and (4) have been postulated[1] as operative in the explosive decomposition of hydrazine.

SZWARC[3] has presented evidence that free radicals are not involved in the

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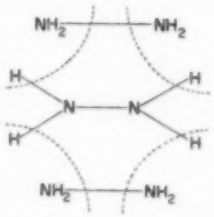
[1] C. H. BAMFORD, *Trans. Faraday Soc.* **35**, 1239 (1939). *Cf.* L. F. AUDRIETH and B. A. OGG, *The Chemistry of Hydrazine* p. 91. John Wiley, New York (1951).
[2] P. J. ASKEY, *J. Amer. Chem. Soc.* **52**, 970 (1930).
[3] M. SZWARC, *Proc. Roy. Soc.* A **198**, 267 (1949).

heterogeneous reaction and has proposed a reaction path in which the decomposition of an activated complex



occurs as indicated on the walls of the reaction vessel.

In order to further elucidate the reaction mechanism, experiments have been carried out on the thermal decomposition of mixtures of nitrogen-15 labelled hydrazine ($H_2{}^{15}N$–$^{14}NH_2$) and normal hydrazine ($H_2{}^{14}N$–$^{14}NH_2$) to determine whether randomization of ^{14}N and ^{15}N occurred in the nitrogen product. It is known that randomization of molecular nitrogen (i.e. ^{15}N–^{15}N and ^{14}N–^{14}N do not exchange) does not occur below 750°C.[4] The results of these studies indicate that reactions involving gaseous radicals are unlikely in the decomposition and are consistent with the SZWARC mechanism.

EXPERIMENTAL

Anhydrous nitrogen-15 labelled hydrazine was prepared from $^{15}NH_4{}^{14}NO_3$ (~32 atom per cent ^{15}N in the ammonium nitrogen and only the ammonium nitrogen is labelled) by a method similar to that described by RICE[5]. Anhydrous normal hydrazine was prepared from 95 per cent hydrazine by a method described by the same author. Both the normal and the enriched hydrazine were stored separately in evacuated containers at −80°C and prior to use were further purified by pumping off traces of impurities at −80°C.

Since the labelled hydrazine was prepared from labelled ammonia the distribution of nitrogen atoms in it, except for negligible isotopic effects, should be random. Mass spectrometric analysis of the nitrogen gas resulting from the thermal decomposition of the labelled hydrazine showed that the distribution of ^{14}N–^{14}N, ^{14}N–^{15}N and ^{15}N–^{15}N was random and the atom fraction of ^{15}N was found to be 0·319.

The exchange experiments were carried out by mixing approximately equal parts of gaseous normal and enriched hydrazine. The mixture was added to a Pyrex reaction vessel at a total pressure of 10–12 mm of mercury and at temperatures between 270° and 330°C. The temperature of the bath during a run was kept constant to ±0·3°C. The half time of decomposition in this temperature range is 4–12 min so that the decomposition according to equation (1) is essentially complete in 1 hr. The reaction products were then passed through a trap cooled with liquid nitrogen to remove ammonia and any unreacted hydrazine and the nitrogen that was collected was analysed for mass 28, mass 29 and mass 30 mass-spectrometrically.

Because hydrazine is absorbed on glass walls and stop-cock grease the possibility exists that on transfer of the hydrazine mixture (normal and labelled) to the reaction vessel, exchange of gaseous and wall hydrazine will occur and alter the measured ratio of labelled to normal hydrazine. In order to obviate this difficulty the ratio r of normal hydrazine/labelled hydrazine in the reaction vessel was calculated from the mass spectrometric data. The value of r is given by $r = ((x_1 - x)/(x - x_0)$ where x_1 is the atom fraction ^{15}N in the labelled hydrazine ($x_1 = 0{\cdot}319$), x_0 the corresponding atom fraction in normal hydrazine (x_0, normal abundance of ^{15}N taken as 0·0037[6]) and x is the atom fraction ^{15}N in the nitrogen gas resulting from the decomposition of the hydrazine mixture. x is calculated from the measured mass-spectral peak heights P_{28}, P_{29}, and P_{30} of the species ^{14}N–^{14}N, ^{15}N–^{14}N and ^{15}N–^{15}N respectively.

[4] G. C. JORIS and H. S. TAYLOR, *J. Chem. Phys.* **7**, 893 (1939).
[5] F. O. RICE and F. SCHERBER, *J. Amer. Chem. Soc.* **77**, 291 (1955).
[6] A. O. NIER, *Phys. Rev.* **77**, 789 (1950).

Vol. 15 1960

RESULTS AND DISCUSSIONS

The ratios of the nitrogen molecular species ^{15}N–$^{15}N/^{14}N$–^{14}N and ^{15}N–$^{14}N/^{14}N$–^{14}N resulting from the thermal decomposition of hydrazine for the conditions of no randomization and randomization of nitrogen atoms may readily be calculated since the nitrogen atoms are randomly distributed in both the labelled and normal hydrazine The result, in terms of the ratio r, and the atom fractions of labelled and normal hydrazine, is

1. No randomization of N atoms

$$\frac{^{15}N\text{–}^{15}N}{^{14}N\text{–}^{14}N} = \frac{x_0^2 r + x_1^2}{(1-x_0)^2 r + (1-x)^2} \quad ; \quad \frac{^{15}N\text{–}^{14}N}{^{14}N\text{–}^{14}N} = \frac{2[x_0(1-x_0)r + x_1(1-x_1)]}{(1-x_0)^2 r + (1-x_1)^2}$$

2. Randomization of N atoms

$$\frac{^{15}N\text{–}^{15}N}{^{14}N\text{–}^{14}N} = \frac{(x_0 r + x_1)^2}{[r(1-x_0) + (1-x_1)]^2} \quad ; \quad \frac{^{15}N\text{–}^{14}N}{^{14}N\text{–}^{14}N} = \frac{2(x_0 r + x_1)}{r(1-x_0) + (1-x_1)}$$

The results of a typical mass-spectrometric analysis of the nitrogen gas formed from the decomposition of the hydrazine mixture are given in Table 1. Similar results were obtained at 280°C.

TABLE 1.—ISOTOPIC ANALYSIS OF N_2 FROM THE DECOMPOSITION OF HYDRAZINE AT 323°C

$$r = \frac{\text{normal hydrazine}}{\text{labelled hydrazine}} = 0{\cdot}95$$

Mass ratio	30/28	29/28
Species ratio	^{15}N–$^{15}N/^{14}N$–^{14}N	^{15}N–$^{14}N/^{14}N$–^{14}N
Measured ratio from mass-spectra data	0·0727	0·313
Calculated ratio for no randomization of N atoms	0·0724	0·314
Calculated ratio for randomization of N atoms	0·0394	0·384

The data of Table 1 show unequivocally that there is no randomization of nitrogen atoms in the decomposition. Lack of randomization clearly signifies that the N–N bond existing in molecular nitrogen has not broken during the process of decomposition.

SZWARC has objected to a free radical mechanism on kinetic grounds. He showed that the rate of formation of dibenzyl in the reaction of hydrazine and toluene between 650°–850°C was independent of the glass surface area of the reaction vessel. Since this reaction depends on the formation of amino radicals from the homogeneous decomposition of hydrazine the lack of a heterogeneous contribution is a serious criticism of the radical mechanism.

The radical mechanism (equations 2, 3, 4) will be examined in light of the non-randomization results. Essentially two arguments against this path when (3) and (4) are homogeneous gaseous reactions will be given. Firstly, reversal of reaction (2) would lead to partial or complete randomization of nitrogen atoms if reaction (3) were not sufficiently rapid relative to $2NH_2 \rightarrow N_2H_4$. Although the reaction might require a third body or wall, it occurs with little or zero activation energy and is thus expected to be rapid. Quantitatively according to this mechanism

the ratio p, of the rate of disappearance of amino radicals by their homogeneous recombination (rate constant k_{-2}) to their disappearance by reaction (3) is given by $p = 2k_{-2}(NH_2)/k_3(N_2H_4)$. From the randomization data, providing that this mechanism is operative, p must be less than 0·05. Since the decomposition of hydrazine is first order we can show that $(NH_2) = 2k_1/3k_3$ and $p = 4k_1k_{-2}/3k_3^2\,(N_2H_4)$ where k_1 is the experimentally determined first order constant for the decomposition and is about 2×10^{-8} sec^{-1} at 323°C under the surface conditions of our experiments. The initial hydrazine concentrations in the randomization experiments is about 2×10^{-4} mole/l. so that p is approximately $10k_{-2}/k_3^2$. Although p cannot be calculated from these constants it may be possible to obtain an order of magnitude value using the constants for somewhat analogous hydrocarbon free radical reactions. For the reactions $CH_3 + CH_3 \rightarrow C_2H_6$ k_{-2}) and $CH_3 + RH \rightarrow R + CH_4$ (k_3) the following values are obtained for p.[7]

R	p
CH_3—CH_3	10,000
CH_2=CH	2,000
NH_2	5,000
CH_3—NH	200

all of which are considerably greater than the maximum allowable value of 0·05. Secondly, BIRSE and MELVILLE[8] studied the decomposition of hydrazine at 200°C in the presence of parahydrogen and found that no *para–ortho* conversion occurred.* Since the conversion is very sensitive to the presence of free radicals the lack of conversion has been cited[3] as further evidence against the radical mechanism. The lack of conversion does not eliminate the possibility of free radicals, but rather establishes a low upper limit to their concentration. According to the radical mechanism the steady state rate of production of nitrogen is $2k_4(N_2H_3)^2 = k_1(N_2H_4)/3$ or $(N_2H_3)^2 = k_1\,(N_2H_4)/6k_4$. The value of k_1 at 200°C and the hydrazine concentration may be obtained from the data of BIRSE and MELVILLE. If the maximum value of k_4 is taken as 10^{11} l. $mole^{-1}$ sec^{-1} (i.e. steric factor of unity and activation energy of zero) the minimum allowable concentration of N_2H_3 is between 10^{-9} and 10^{-10} mole/l. which is probably within the limits detectable by *ortho–para* conversion.† Further if reaction

* The small amount of *para* conversion observed may be explained by the production of normal hydrogen from the decomposing hydrazine.[9]

† A rough estimate of the sensitivity of the *o–p* conversion for N_2H_3 radicals may be obtained by assuming that the conversion occurs only through the steady state concentration of hydrogen atoms produced in the reactions.

$$H_2 + N_2H_3 \rightarrow N_2H_4 + H \qquad k_5$$
$$H + N_2H_4 \rightarrow NH_2 + NH_3 \qquad k_6$$

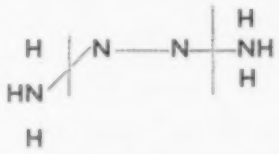
The radical concentration ratio $(N_2H_3)/(H)$ is $k_6\,(N_2H_4)/k_5(H_2)$ which for the BIRSE and MELVILLE experimental conditions reduces to $0{\cdot}2\,k_6/k_5$. k_6 from the latter's results is about 10^8 l. $mole^{-1}$ sec^{-1} at 200°C. If the steric factor, P and activation energy for k_5 is the same as for the reaction $CH_3 + H_2$ ($P = 10^{-5}$, $E = 9200$)[10a] $(N_2H_3)/(H)$ is about 30. For the reaction $C_2H_5 + H_2$ $P = 10^{-5}$ and $E = 12000$,[10b] and using these values to calculate k_5, $(N_2H_3)/(H)$ is 600. The sensitivity of the *o–p* conversion is about 10^{-14} mole/l. H atoms so that on the basis of these comparisons a sensitivity for (N_2H_3) of about 3×10^{-12} to 6×10^{-12} is obtained.

[7] E. W. R. STEACIE, *Atomic and Free Radical Reactions*, Vol. 2, p. 500. Reinhold, New York (1954).
[8] E. A. BIRSE and H. W. MELVILLE, *Proc. Roy. Soc.* A **175**, 164 (1940).
[9] M. SZWARC, see ref. 3, p. 283, footnote.
[10] E. W. R. STEACIE *Atomic and Free Radical Reactions* Vol. 2,[a] p. 531,[b] p. 573. Reinhold, New York (1951).

Vol. 15 1960

(4) is to occur with no randomization of nitrogen atoms in the nitrogen product then the ammonia must be derivable from only one N_2H_3 molecule and the molecular nitrogen from the other reacting N_2H_3 molecule. A reaction of this type would require an oriented transition complex so that the steric factor would be small. In addition a considerable activation energy is necessary to rupture the N–N bond of one of the reacting radicals. It is thus follows that for the case of no randomization the N_2H_3 concentration would be much larger (at least a few orders of magnitude) than that calculated under the assumption of maximum value for k_4 and this concentration should be readily detectable by *ortho–para* conversion.

Reaction (4) can occur with zero or small activation energy and perhaps not too small a steric factor via a transition complex involving free radical recombination in this manner



The energy required to rupture the two nitrogen bonds as shown in the figure being derived from the making of the molecular nitrogen bond (225 kcal/mole). This path would, of course, lead to partial randomization of the nitrogen atoms in the molecular product and thus does not occur. It is difficult to find other decomposition paths involving gaseous species and consistent with both the stoicheiometry of equation (1) and the non-randomization of nitrogen atoms in the molecular nitrogen that are not subject to serious objections.

The SZWARC mechanism given in the introduction is, of course, consistent with the non-randomization result and with the failure of the decomposition species to catalyse the *para–ortho* conversion. An experiment in which normal hydrazine was allowed to decompose in a reaction vessel whose walls were previously saturated with enriched hydrazine was performed to test whether the reaction path involved the abstraction of hydrogen from adsorbed hydrazine. The reaction was allowed to proceed until only 5 per cent of the hydrazine was decomposed and it was found that the atom fraction of ^{15}N in the nitrogen was as high as 18 per cent. This result shows that the nitrogen is indeed formed from adsorbed hydrazine and is consistent with the mechanism proposed by SZWARC.

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INTERCONVERSION OF BORANES—I

A KINETIC STUDY OF THE CONVERSION OF TETRABORANE-10 TO PENTABORANE-11

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(*Received* 4 *January* 1960)

Abstract—Kinetic studies of conversion of B_4H_{10} to B_5H_{11} are reported. The rate equation

$$\text{Rate} = 6{\cdot}5 \times 10^{15} \exp(-24300/RT)(B_4H_{10})$$

is interpreted in terms of the two step reaction

$$B_4H_{10} \rightarrow B_4H_8 + H_2$$
$$B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3$$

wherein the first step is rate limiting.

Application of semitopological equations (modified to treat vacant orbital structures) leads to two satisfactory structures for B_4H_8.

IN the early studies by STOCK and co-workers on the chemistry of boron hydrides,[1] various members of this interesting series were isolated from the products of hydrolysis of magnesium boride. However, subsequent to the discovery by SCHLESINGER and co-workers of simplified procedures for the preparation of diborane,[2] the thermal decomposition of diborane became the preferred method of preparation of higher boranes. The pathway followed in the conversion of diborane to higher boranes is undoubtedly complex but two previous studies have served to elucidate some of the overall aspects of the reaction.[3] Nevertheless, more detailed study of individual conversion reactions is certainly essential to a basic understanding of the processes involved.

In 1933 BURG and SCHLESINGER described the preparation of pentaborane-11 from diborane[4] and suggested that the equilibrium

$$2\,B_4H_{10} + B_2H_6 \rightleftharpoons 2\,B_5H_{11} + 2\,H_2 \qquad (1)$$

was of some importance. The possible importance of this reaction in the interconversion of boranes motivated us to undertake a study of the kinetics of the reaction in the forward direction.

EXPERIMENTAL

The apparatus and methods employed in the purification of materials, and the isolation and identification of volatile products have been adequately described by SANDERSON[5]. All pressures are given in millimetres of mercury and all gas volumes, unless otherwise stated, are given in cubic centimetres of gases at 0° and 760 mm pressure. Diborane was prepared by the reaction of lithium aluminium hydride with boron trichloride in diethyl ether solution and was purified as necessary before each run by passing it through a trap maintained at −135°.

* Reprint requests should be directed to this author, Department of Chemistry, Box C, Indiana University, Bloomington, Indiana.

[1] A. STOCK, *Hydrides of Boron and Silicon.* Cornell University Press, Ithaca (1933).
[2] H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **53**, 432 (1931); H. I. SCHLESINGER and H. C. BROWN, *Ibid.* **75**, 195 (1953); A. E. FINHOLT, A. C. BOND and H. I. SCHLESINGER, *Ibid.* **69**, 1199 (1947).
[3] R. P. CLARKE and R. N. PEASE, *J. Amer. Chem. Soc.* **73**, 2132 (1951); J. K. BRAGG, L. W. MCCARTY and F. J. NORTON, *Ibid.* **73**, 2137 (1951).
[4] A. B. BURG and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **55**, 4009 (1933).
[5] R. T. SANDERSON, *High Vacuum Manipulation of Volatile Compound.* John Wiley, New York (1948).

Vol. 15 1960

Tetraborane-10 was prepared by passing a stream of diborane mixed with helium through a silent discharge following the procedure of KOTLENSKY and SCHAEFFER[6]. Pure tetraborane-10 was recovered by distillation through a −95° trap and condensation in a −135° trap. Vapour pressure of the tetraborane used was 387 mm at 0° compared with the reported value of 386·8 mm. Both diborane and tetraborane-10 were stored at liquid nitrogen temperature to prevent their decomposition and were purified again prior to each series of experiments.

Procedure. Kinetic studies were carried out in Pyrex bulbs equipped with a seal-off constriction and a simple break-off tip. Samples of the purified reactants were condensed into the reaction bulb at −196° and sealed from the vacuum system. After sealing from the system the bulbs were allowed to reach room temperature and then quickly immersed in a bath of the appropriate temperature. A thermostated mineral oil-bath which maintained temperature constant within 0·05°C was used in all cases. After samples had been immersed for the desired length of time, they were removed from the bath, quickly wiped of excess oil, and immediately quenched in an ice-bath for approximately 15 sec and then transferred to a liquid nitrogen bath. The bulbs were then sealed to the vacuum apparatus through the break-off and opened to the system. Hydrogen was removed by an automatic Toepler pump and the volume of hydrogen produced measured in a calibrated system. All volatile boranes were transferred to the fractionation system for separation. Subsequent to the reaction and removal of products, the volume of each bulb was obtained by determining the weight of the distilled water required to fill it.

Diborane was isolated from the reaction products by fractionation through a −135° trap. Tetraborane-10 and pentaborane-11 were separated by fractionation through a −95° trap. The volumes and the characteristic vapour pressures of the separated fractions were individually determined. The effectiveness of the separation procedure was demonstrated by the quantitative recovery of the proper amounts from a known mixture of diborane, tetraborane-10 and pentaborane-11.

RESULTS

The reaction of tetraborane-10 with diborane was found to be independent of diborane pressure and first order in tetraborane-10. No substantial change in the rate of the reaction was produced by the introduction of Pyrex glass wool into the reaction vessel.* Table 1 presents the experimental data at various temperatures.

At higher temperatures, particularly at longer time intervals, some divergence of the rate constant was observed. Apparently a competing reaction causes some interference under these conditions. In ocasional experiments rate constants considerably different from the expected values were obtained. However, almost without exception in such cases an inadequate separation or loss of products was indicated by a poor boron hydride balance. Only those experiments in which the total final volume of tetraborane-10 and pentaborane-11 was within 5 per cent of the initial tetraborane-10 volume (required by the stoicheiometric relation to be equal) were employed in subsequent analysis. Best rate constants for a given temperature were derived by applying a least squares treatment to a first order rate-expression. At 100° and 110° calculated rate constants decreased with increasing time. Thus at 100° the rate constant fell from 0·367 min^{-1} at 3 min to 0·14 min^{-1} at 13 min. However, in 13 min nearly 90 per cent of the original tetraborane had been consumed and on consideration of the earlier evidence of BURG and SCHLESINGER that the system reaches equilibrium, it is clear that a major factor in the variation of rate constant with time is the increasing importance of the reaction in the back direction. A rough extrapolation of the experiments at 100° to zero time suggests a rate constant between 0·4 and 0·5, compared with a value of 0·47 obtained by calculation from the lower temperature using the observed

* This experiment was carried out by Mr. G. BRENNAN whose assistance is gratefully acknowledged.

[6] W. V. KOTLENSKY and R. SCHAEFFER, *J. Amer. Chem. Soc.* **80**, 4517 (1958).

heat of reaction. Similarly, the calculated value at 110° is 1·0 min^{-1} compared with approximately 0·7 min^{-1} measured at 3 min. Crude equilibrium constants for reaction (1) might be estimated from the data presented in Table 1.

A plot of the logarithm of the rate constant vs. the reciprocal of the temperature is shown in Fig. 1 for the lower four temperatures studied. The activation energy derived by least mean squares treatment of the rate constant summarized in Table 2 leads to a value of 24·3 kcal for the heat of activation.*

TABLE 1.—REACTION OF TETRABORANE-10 WITH DIBORANE

Time (min)	Temp. (°C)	Volume B_4H_{10} initial	Volume B_2H_6 initial	Volume B_4H_{10} final	k (min^{-1})
8·0	72·5	7·534	18·06	5·728	0·0342
10·0	72·5	3·667	7·253	2·479	0·0391
12·0	72·5	6·067	18·16	3·919	0·0364
14·0	72·5	4·198	14·57	2·453	0·0384
16·0	72·5	5·145	7·244	2·942	0·0349
18·0	72·5	4·030	12·84	2·033	0·0380
20·0	72·5	4·317	8·625	2·059	0·0370
5·0	85·4	4·674	9·189	2·393	0·134
8·0	85·4	4·406	9·282	1·614	0·126
10·0	85·4	4·858	9·069	1·397	0·125
12·0	85·4	3·790	8·581	0·898	0·120
3·0	92·9	4·748	10·99	2·104	0·271
4·0	92·9	5·587	13·09	1·781	0·286
5·0	92·9	4·748	15·39	1·104	0·292
6·0	92·9	5·618	12·09	1·280	0·247*

* Additional data at this and higher temperatures may be found in the M.S. thesis of J. A. DUPONT[7].

DISCUSSION

It is clear from the observed rate expression

$$\text{Rate} = k(B_4H_{10})$$

that the rate determining step in the reaction of tetraborane-10 with diborane involves only the tetraborane molecule. The two step reaction

$$B_4H_{10} \rightarrow B_4H_8 + H_2 \quad (2)$$

$$B_4H_8 + B_2H_6 \rightarrow B_5H_{11} + BH_3 \quad (3)$$

(if loss of hydrogen in the first step is rate controlling) is an attractive one. In a study reported subsequent to the completion of this work, PEARSON and EDWARDS[8] suggest the rate controlling step is the elimination of the BH_3 group from tetraborane-10. It is possible that an accidental ratio of rate constants in their mechanism might lead to kinetics zero order in diborane. Evidence from other sources indicates, however, that B_3H_7 reacts rapidly with diborane to give B_4H_{10}. Thus, diborane should inhibit the present reaction if their mechanism were followed.

* It is interesting to note that the heat of activation obtained here is nearly that observed by PEARSON and EDWARDS[8] for the thermal decomposition of tetraborane-10 although the rate of that reaction is about one order of magnitude lower.

[7] J. A. DUPONT, M.S. Thesis, Iowa State University (1958).

[8] R. K. PEARSON and L. J. EDWARDS, Abstracts of Papers presented at the 132nd Meeting of the American Chemical Society, New York, 1957, p. 15N.

Vol. 15 1960

Tetraborane-8, postulated here as a reaction intermediate, has never been isolated although PEARSON and EDWARDS postulated it as an intermediate in pyrolysis of B_4H_{10} *in the absence* of diborane. As a result of the extensive experimental and

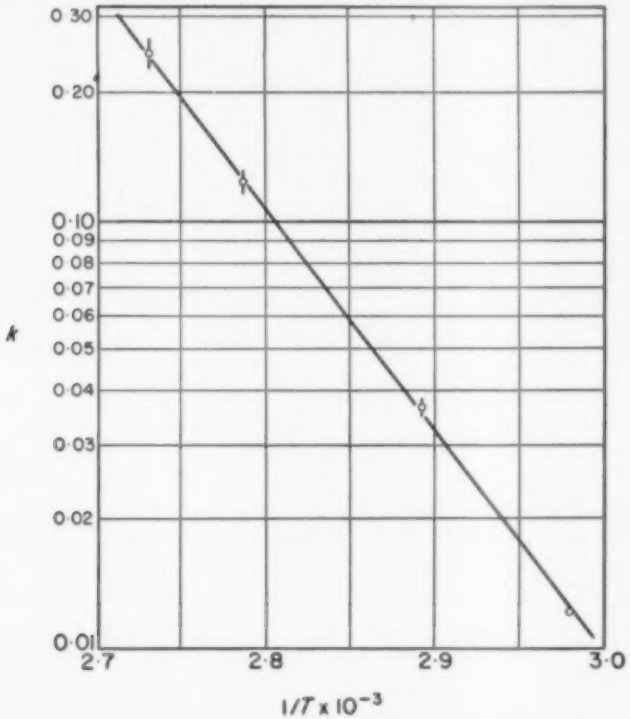


FIG. 1.—Arrenhius plot of the first order rate constants.

TABLE 2.—CALCULATED FIRST ORDER RATE-CONSTANTS FOR $B_4H_{10} + \frac{1}{2}B_2H_6 \rightarrow B_5H_{11} + H_2$

Temp (°C)	k (min^{-1})	$k_{calc} = 6{\cdot}50 \times 10^{13} \exp(-24300/RT)$
92·5	0·248	0·245
85·4	0·123	0·127
72·5	0·037	0·036
62·5	0·0124	0·0126

theoretical work of LIPSCOMB[9], a moderately detailed consideration of the structure of such an intermediate can be undertaken. Application of the topological theory of LIPSCOMB and DICKERSON[10] leads to possible structures of 4020, 3111 and 2202 types.* All attempts to derive a structure of one of these types based on an icosahedral

* In this notation the figures are $s\ t\ y\ x$ where s is the number of hydrogen bridges, t is the number of three centre bonds involving only boron, y is the number of single boron–boron bonds and x is the number of boron–hydrogen terminal bonds in excess of one per boron (and hence essentially the number of BH_2 groups per molecule).

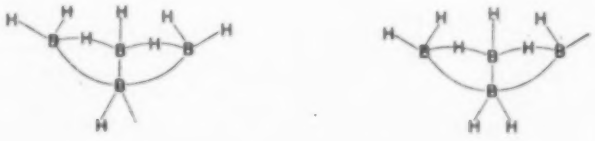
[9] See for a general review, W. N. LIPSCOMB, *Advances in Inorganic Chemistry and Radiochemistry* Vol. I, Chap. 3. Academic Press, New York (1959).

[10] A. R. DICKERSON and W. N. LIPSCOMB, *J. Chem. Phys.* **27**, 212 (1957).

fragment are unsatisfactory. Of course, pentaborane-9 is a well known borane molecule not based on icosahedral geometry and no guarantee exists that other moecules might not likewise utilize some other framework. Thus, a simple and symmetrical tetrahedral B_4H_8 of the 4020 type may be constructed. Further consideration should be given, however, to the possibility that an icosahedral framework is required.

In early speculations concerning the structure of boranes, it was not uncommon to postulate borane structures in which boron formed only three bonds, particularly so on consideration of the Lewis acid properties displayed by most boranes. More recently, the success of the valence bond three-centre orbital picture presented by EBERHARDT, *et al.* (and more refined molecular orbital considerations) served to divert attention from open orbital configurations. Certainly the simple BH_3 group so frequently postulated in boron chemistry must possess one substantially unfilled orbital. (Even the recent treatment of RICE places only slight electron density in the fourth orbital.[11]) No fundamental reason can be given for omitting consideration of open orbital structures as reactive intermediates.

The topological equations of LIPSCOMB and DICKERSON may be readily modified. For the borane of general formula B_pH_{p+q}, hydrogen balance still requires that $s + x = q$. Similarly, electron balance in the molecule requires $t + y = p - q/2$. However, derivation of an orbital balance equation leads to the alteration $s + t = p - 1$ for a molecule with a single vacant orbital. Application of these equations to the tetraborane-8 molecule suggests that structures of the 1203, 2112 and 3021 types must be considered. Tetraborane-10 itself contains only two BH_2 groups and it appears unlikely that loss of hydrogen should produce more such groups. Moreover, consideration of possibilities based on an icosahedral fragment fails to yield a satisfactory structure of the 1203 type. Similarly, no satisfactory 3021 structure may be drawn (indeed such a structure is impossible if one accepts the additional assumption of topological theory that at least a mirror plane of symmetry is required). Two structures of the 2112 type can be drawn with two possible isomers of each structure. Both appear to be satisfactory within the limits of the topological framework and indeed appear to be the only satisfactory structures for a B_4H_8 molecule based on an icosahedral framework. These structures are shown below.



Not only is one led to a single pair of satisfactory structures for a tetraborane-8 molecule by the above considerations but moreover, the structures thus derived allow simple stereochemical interpretation of the reaction path. The *net* structural alteration which must occur to convert tetraborane-10 to the above tetraborane-8 structures is elimination of bridge protons from one side of the molecule. However, it would seem more suitable to eliminate one bridge proton and one proton from the basal boron since theoretical considerations of LIPSCOMB and others[9] would seem to call for more hydride like character of bridge hydrogens and more proton like character of terminal

[11] W. L. CLINTON and B. RICE, *J. Chem. Phys.* **30**, 542 (1959).

Vol. 15 1960

hydrogens.* The resulting tetraborane molecule is isomeric with the one shown above, with only a slight rearrangement of the type previously postulated by LIPSCOMB[12]. Furthermore, no extensive nor unusual sterochemical changes must be invoked in the reaction of the intermediate with diborane to produce pentaborane-11. Thus, the reaction might follow such a pathway as: Attack of the vacant orbital of the tetraborane-8 molecule at a terminal hydrogen of the diborane molecule with subsequent or simultaneous release of the BH_3 group; attack of the newly introduced boron at the adjacent terminal BH_2 group with formation of a new bridge bond; rearrangement of the adjacent single boron–boron bond and bridge bond to the stable pentaborane-11 structure.

No detailed justification for these stages can be given, but the pathway appears attractive.

Further related studies have been carried out tending to confirm the importance of tetraborane–8 as an intermediate in this reaction. These studies will be reported elsewhere in the near future.[13]

Acknowledgements—The authors wish to acknowledge several helpful discussions of this problem with Professors W. L. MEYER and V. J. SHINER, Department of Chemistry, Indiana University. The comments of one of the referee's also served to improve the paper substantially

* We need not enter here the argument concerning the relative polarity of the two types of hydrogen. The reverse polarity to that chosen here would serve equally well. Our argument merely suggests use of two hydrogens of opposite polarity.

[12] W. N. LIPSCOMB, *J. Inorg. Nucl. Chem.* **11**, 6 (1959).

[13] Work by G. BRENNAN and R. SCHAEFFER. A preliminary report was published as *WADC Technical Note* 59-258 under Contract No. AF 33 (616)-5827.

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 316 to 319. Pergamon Press Ltd.

A GAS–CHROMATOGRAPHIC STUDY OF THE DIBORANE PYROLYSIS

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(*Received* 26 *January* 1960)

Abstract—The use of gas–liquid chromatographic techniques for the study of volatile reactive inorganic substances is illustrated by an investigation of diborane pyrolyses over a range of temperature from 50 to 188°C.

WHEN diborane is heated alone at temperatures between about 70 and 200°C, it decomposes slowly into hydrogen, a mixture of more complex volatile hydrides, and a solid polymer of variable composition.[1–3] The reaction has been followed by the rise in pressure,[2,3] by the pressure of hydrogen produced, and by mass-spectrometry.[3] This paper describes the study of the reaction by gas–liquid chromatography. This method of analysis is particularly suitable for the detection and determination of small amounts and small proportions of volatile substances. Its use for the separation of boron hydrides has been reported by LITTLEWOOD[4], and by KAUFMAN *et al.*[5]

APPARATUS AND EXPERIMENTAL TECHNIQUE

Chromatographic apparatus. This was similar to that already described.[6] Column and katharometer were contained in a vapour jacket, which for the analysis of boron hydrides contained ether at 34·5°C. Oxygen-free nitrogen, dried with magnesium perchlorate, was used as carrier gas. Since the various reaction products are easily separated, only a short column is required, and indeed a short column is desirable in order to avoid long residence times for unstable hydrides within it. In most of the analytical work, the column was 40 cm in length, 5 mm internal diameter, and contained 0·59 g of Silicone 702 (Midland Silicones Ltd.) supported on 1·47 g. of Celite 535 (Johns–Manville). A column capable of handling up to about 0·5 g of crude diborane per run was also used to purify the diborane used for the pyrolyses; it was 150 cm in length, 12 mm internal diameter, and contained 18·9 g of Silicone 702 on 47·1 g of Celite.

Apparatus. Crude diborane was prepared by the method of SCHLESINGER *et al.*[7] The apparatus for the preparation, purification and pyrolysis of diborane, and for the analysis of reaction products was arranged so that all handling was carried out *in vitro*, either *in vacuo* or in a stream of the carrier gas (Fig. 1). Pyrolyses were performed in a glass vessel A of about 500 ml capacity, held at the required temperature by a vapour jacket. As pyrolysis proceeded, samples were collected at known intervals in the previously-evacuated sampling vessel B, which was small (about 10 ml) compared to A, and though the abstraction of each sample produced a measurable drop in the pressure measured by the manometer C, it did not sensibly change the rate of reaction. The sample in B was frozen at liquid oxygen temperature, and hydrogen was pumped off; the remainder was then transferred *in vacuo* to the trap D. The normal path of the carrier gas is through stopcocks G, H and I. The sample

* Present address: Imperial Chemical Industries, Billingham.
† Present address: Department of Chemistry, University of Durham, Newcastle-upon-Tyne.

[1] A. STOCK, *Hydrides of Boron and Silicon.* Cornell University Press (1933).
[2] R. P. CLARKE and R. N. PEASE, *J. Amer. Chem. Soc.* **73**, 2132 (1951).
[3] J. K. BRAGG, L. V. MCCARTY and F. J. NORTON, *J. Amer. Chem. Soc.* **73**, 2134 (1951).
[4] A. B. LITTLEWOOD, *Analyst*, **81**, 55 (1956).
[5] J. J. KAUFMAN, J. E. TODD and W. S. KOSKI, *Analyt. Chem.* **29**, 1032 (1957).
[6] A. B. LITTLEWOOD, C. S. G. PHILLIPS and D. T. PRICE, *J. Chem. Soc.* 1480 (1955).
[7] H. I. SCHLESINGER, H. C. BROWN, J. R. GILBREATH and J. J. KATZ, *J. Amer. Chem. Soc.* **75**, 195 (1953).

Vol. 15 1960

was introduced to the column by operating G, H and E so that carrier gas was deflected to sweep out D. After passage through the column, components were trapped at liquid oxygen temperature either separately (traps L, M, N and O) or together (trap J). Individual hydrides could then be transferred *in vacuo* to other analytical apparatus when required. When all the components were condensed together at the outlet of the column, the chromatogram could be repeated by removing the liquid oxygen and reversing the flow of carrier gas by turning G and I. In cases where there was not time to chromatograph one sample before taking another, it could be transferred *in vacuo* to storage traps (not shown) and chromatographed later.

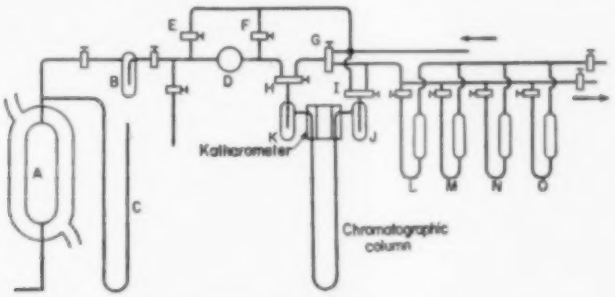

FIG. 1.—Diagram of apparatus.

Analytical methods. Three methods were used to identify the components emerging from the column.

(a) *Complete pyrolysis.* The component producing a peak was heated to bright red heat in a thick Pyrex tube, and the number of hydrogen atoms produced per molecule of the component determined from the rise in pressure.

(b) *Hydrolysis.* Diborane was analysed by hydrolysis, followed by measurement of the volume of hydrogen produced.

(c) *Microeffusiometry.* A microeffusiometer similar to that of NASH[8] was used to determine the molecular weights of components. Calibration with substances of known molecular weights showed that molecular weights could be determined with an accuracy of 2 per cent (mean deviation), as claimed by NASH; by careful adjustment so that the apparatus worked at the lowest possible pressures, the molecular weights of quantities down to six micromoles could be determined.

EXPERIMENTAL RESULTS

Chromatographic results. In general, the chromatogram obtained from a pyrolysed sample of diborane had four peaks, as in the example shown in Fig. 2. These were identified in order of increasing retention volume as diborane, tetraborane, pentaborane and dihydropentaborane. Specific retention volumes[9] (V_g values[6]) for Silicone 702 oil at 34·5°C were found to be 12, 65, 254 and 355 ml g^{-1}.

In order to determine whether any hydrides were decomposing in the column, samples of mixed boron hydrides were passed back and forth through the column, using the reversing procedure described above, and the areas of the peaks on each successive chromatogram were measured. In the case of diborane, tetraborane and pentaborane, no decrease in area occurred in at least six passages through the column. However with dihydropentaborane, successive passages led to a diminution in area of 10 ± 2 per cent per passage. This corresponds to a half-life of the order of 100 min for dihydropentaborane in the column at 34·5°C. When pure dihydropentaborane was run back and forth, small peaks corresponding to tetraborane and pentaborane were

[8] L. K. NASH, *Analyt. Chem.* **20**, 258 (1948).
[9] D. AMBROSE, A. I. M. KEULEMANS and J. H. PURNELL, *Analyt. Chem.* **30**, 1582 (1958).

observed on the second passage and grew after succeeding passages. Since none appears after the first passage, the decomposition occurs in the column and not in the katharometer, through the reference half of which pure dihydropentaborane must pass on its first passage through the column. In contrast to the results of KAUFMAN *et al.*[5] we do not find that the decomposition of dihydropentaborane is too rapid to be able to make measurements, and we find no diborane in the decomposition products. Recently BOONE and BURG[10] have shown that the decomposition of dihydropentaborane in

FIG. 2.—A typical chromatogram.

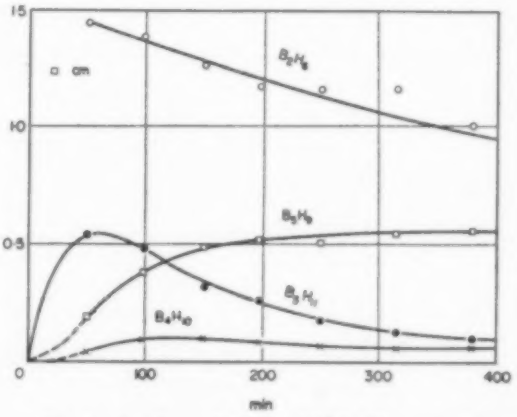

FIG. 3.—Pyrolysis of B_2H_6 at 111°C. Chromatogram peak areas plotted against time.

the condensed phase at low temperatures is sharply affected by liquid catalysts, especially if they are basic, and this may account for the differences in the behaviour of dihydropentaborane.

Kinetic results. Diborane was pyrolysed at temperatures ranging from 50 to 188°C. At 50°C no reaction could be detected after 5 hr. At higher temperatures the reaction, was easily measurable, and was directly demonstrable by the continuously increasing pressure in the pyrolyser. Samples were abstracted at intervals and chromatographed, and the areas of the peaks of diborane and of the higher hydrides were plotted against time. In general the plots resembled that in Fig. 3, which gives the results for 111°C. The area of a peak due to any one hydride is proportional to its mass, and the proportionality constants between area and mass could be shown to be very approximately the same for B_4H_{10}, B_5H_9 and B_5H_{11}, so that the areas in Fig. 3 are approximately proportional to weight proportions. At the same time as the higher hydrides were formed, hydrogen was produced, together with crystals of a slightly volatile compound (presumably decaborane) which condensed in the cool tubes leading to the pyrolyser, and a yellow deposit which collected largely on the bottom of the pyrolyser.

[10] J. L. BOONE and A. B. BURG, *J. Amer. Chem. Soc.* **80**, 1519 (1958); **81**, 1766 (1959).

Vol. 15 1960

The effect of increase in temperature was to compress the abscissa of Fig. 3 but not to alter the overall shape of the curves. The first product of pyrolysis is always dihydropentaborane, and though only a few runs showed dihydropentaborane without any pentaborane or tetraborane, the plots of the type shown in Fig. 3 suggest that B_5H_{11} is the only hydride which is formed initially. Measurements from plots of composition against time show that the rate of formation of pentaborane is almost exactly proportional to the concentration of dihydropentaborane, and that the same is true of tetraborane up to the shallow maximum in its concentration. At 157°C pentaborane is completely stable for at least 1 hr, but at 188°C it reaches a maximum concentration after about 25 min, the concentration declining thereafter. At this temperature, if any dihydropentaborane is formed in the early stages of the reaction, its concentration has fallen below the level of detection by the time the first sample was taken. The activation energy of the reaction was measured from the rate of increase of pressure at different temperatures and found to be 29 kcal $mole^{-1}$.

The effect of increase in the initial pressure of diborane was to expand the ordinate of Fig. 3, but not to alter the overall shape of the curves. Pressures from about 12 to 60 cm of diborane were used, and at 111°C the order of the reaction was found to be $1{\cdot}5 \pm 0{\cdot}1$.

The kinetic results are in general agreement with those of BRAGG *et al.*[3] The gas chromatographic analyses however give a more complete picture than the mass-spectroscopic data, showing for example a considerable proportion of tetraborane throughout the reaction.

Acknowledgements—One of us (A. B. L.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant and to the Harmsworth Trust, Merton College, for a senior scholarship. We thank Imperial Chemical Industries for the loan of a recorder.

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 320 to 328. Pergmaon Press Ltd.

SOME INVESTIGATIONS IN THE ZIRCONIUM TETRAFLUORIDE–WATER SYSTEM

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(*Received* 13 *November* 1959)

Abstract—A characteristic property of the fluorides of the heavier metals is the ease with which they form hydrates. For example, D'EYE and his co-workers characterized six hydrates of thorium tetrafluoride[1,2] and two hydrates of zirconium,[3] uranium and plutonium tetrafluoride.[4] Thorium tetrafluoride appears to form two sets of related hydrates; the first by precipitation of the fluoride from a Th^{4+} solution and the second by hydration of anhydrous tetrafluoride. Their formation and inter-relationships probably depend as much on the ability of fluorine and oxygen to form hydrogen bonds as on the occurrence of structural voids due to the tendency of fluorine to form network structures. Hydrogen bonds are present in $CuF_2.2H_2O$[5] for example, whereas in uranium tetrafluoride excess fluorine can be accommodated in lattice voids.[6]

THE zirconium tetrafluoride hydrate system has been re-investigated to characterize new hydrates where possible and to determine their structures. A number of new compounds of the general composition $ZrF_4.xHF.yH_2O$ (where x may be zero) have been identified and their relationships to previously characterized hydrates tentatively established. Information has also been obtained about compounds formed by the hydrolysis of zirconium tetrafluoride.

Vol. 15 1960

EXPERIMENTAL

Preparative

The hydrates were prepared by dissolving zirconium tetrafluoride in 40, 20 or 5 per cent aqueous hydrofluoric acid, if necessary at the boiling point, and evaporating the solutions slowly. The products were separated but kept damp with mother liquor to prevent decomposition. They were subjected to controlled degradation either by allowing them to stand for varying periods over silica gel, anhydrone or caustic soda, or sometimes by heating them in air or in a vacuum.

Hydrolysis

(i) *With water.* Weighed quantities of zirconium tetrafluoride were refluxed with a constant volume of water for periods of 1 min to 8 hr and, after cooling, the solid was separated for chemical analysis and X-ray diffraction studies.

(ii) *With steam.* Weighed amounts of the tetrafluoride, in platinum boats, were placed in a horizontal silica tube heated by an electric furnace. Steam was passed over them at a constant rate and the hydrofluoric acid/steam mixtures were condensed and titrated with standard alkali in order to follow the hydrolyses. The temperatures, measured by a thermocouple placed alongside the sample, ranged from 100–450°C. Attack on the silica by the acid proved to be negligible.

Analysis

(i) *Chemical.* Fluorine was determined pyrohydrolytically by heating to 900°C in a current of steam, condensing the mixture of hydrofluoric acid and steam and titrating with alkali. The residual

[1] R. W. M. D'EYE and G. W. BOOTH, *J. Inorg. Nucl. Chem.* **1**, 326 (1955).
[2] R. W. M. D'EYE and G. W. BOOTH, *J. Inorg. Nucl. Chem.* **4**, 13 (1957).
[3] R. W. M. D'EYE, J. P. BURDEN and E. A. HARPER, *J. Inorg. Nucl. Chem.* **2**, 192 (1956).
[4] J. K. DAWSON, R. W. M. D'EYE and A. E. TRUSWELL, *J. Chem. Soc.* 3922 (1954).
[5] S. GELLER and W. L. BOND, *J. Chem. Phys.* **29**, 925 (1958).
[6] R. D. BURBANK and F. N. BERSEY, U.S.A.E.C. Report K-1280 (1956).

oxide was heated in air and weighed as ZrO_2. Agreement was ±0·5 per cent for both fluorine and zirconium. The water (or oxygen) was obtained by difference.

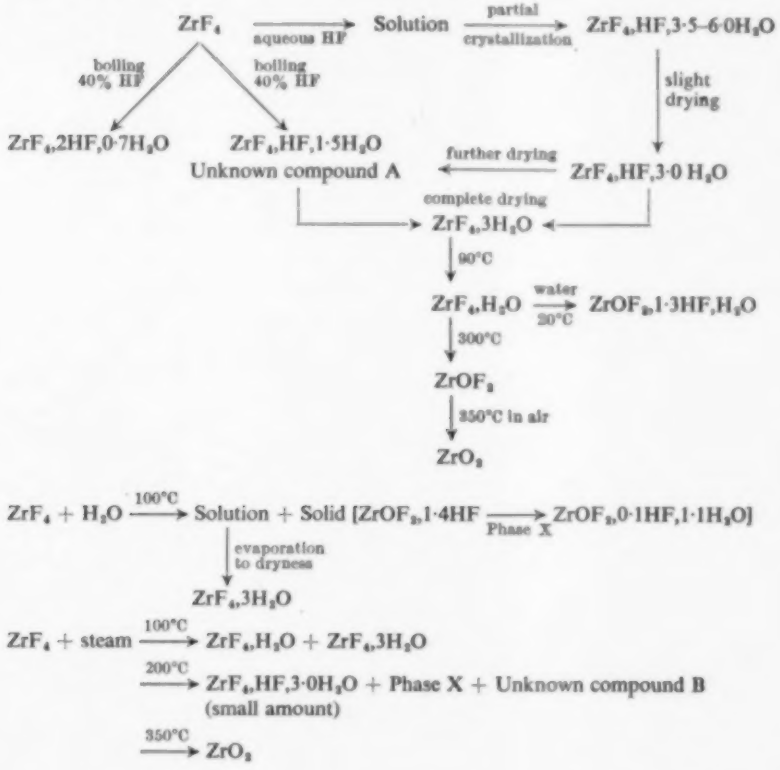
(ii) *X-ray*. Powder diffraction patterns were obtained with a Guinier-type focusing camera. To avoid errors in the measurement of the Bragg angle through film shrinkage a 0·1 mm scale was also photographed on to the film before processing. Single crystal data were obtained from conventional oscillation and equi-inclination Weissenberg photographs.

(iii) *Infra-red*. The infra-red absorption of two compounds were measured in the 1500–4000 cm^{-1} region, the samples being suspended in Nujol and Fluorube-2.

RESULTS

The compounds which have been characterized, and their inter-relationships are shown in Table 1; the method of denoting their composition has no structural significance.

TABLE 1.—PREPARATIVE ROUTES IN THE ZIRCONIUM TETRAFLUORIDE HYDRATE SYSTEM



Intensity and $\sin^2\theta$ values are given for the compounds identified, with values of the cell constants where these have been found (Tables 2–10).

$ZrF_4,2HF,0·7H_2O$ has an hexagonal cell with $a = 8·86$, $c = 5·04$ Å. There are no systematic absences in the reflexions and volume considerations suggest three molecules in the unit cell (Table 2).

$ZrF_4,HF,1·5H_2O$ has a cubic face-centred diffraction pattern, with $a = 5·43$ Å,

superimposed on a generally weaker background pattern. The material is believed to be a single phase, (Table 3).

ZrF_4,HF,3·0H_2O has an orthorhombic cell with $a = 6{\cdot}63$, $b = 8{\cdot}07$, $c = 9{\cdot}89$ Å. Reflexions were present under the following conditions:

$$hkl \text{ when } h + l = 2n$$

TABLE 2.—ZrF_4,2HF,0·7H_2O

I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl
w−	0·0232	0·0234	001	*vw*	0·1238	0·1238	112	*w*+	0·2350	0·2349	411
m	0·0301	0·0302	110	*vw*	0·1308	0·1309	310	*vvw*	0·2403	0·2408	113
m	0·0333	0·0335	101	*vw*	0·1338	0·1339	202	*vvw*	0·2506	0·2509	203
vvw	0·0410	0·0403	200	*w*−	0·1444	0·1442	221	*vvw*	0·2549	0·2547	402
m	0·0535	0·0536	111	*vw*	0·1544	0·1543	311	*w*	0·2719	0·2719	330
m−	0·0636	0·0637	201	*w*−	0·1642	0·1641	212	*vw*−	0·2753	0·2752	501
vw	0·0706	0·0705	210	*m*−	0·1843	0·1842	302	*vw*	0·2809	0·2811	213
vvw	0·0906	0·0906	300			0·1845	401				
w	0·0939	0·0936	002	*vvw*	0·1914	0·1913	320				
		0·0939	211	*w*	0·2150	0·2144	222				
m	0·1141	0·1140	301			0·2147	321				
vw	0·1209	0·1208	220	*vvw*	0·2200	0·2207	103				
				vw	0·2245	0·2245	312				

TABLE 3.—ZrF_4,HF,1·5H_2O

I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	hkl
m−	0·0107			*vvw*	0·1051			*m*	0·2211	0·2211	311
vw	0·0123			*vvw*	0·1097			*vvw*	0·2292		
w	0·0231			*vw*	0·1223			*vvw*	0·2347		
m−	0·0309			*vw*	0·1359			*vw*	0·2414	0·2412	222
m	0·0356			*vw*+	0·1424			*vw*−	0·2584		
w+	0·0371			*vw*+	0·1471			*vw*−	0·2778		
vw	0·0434			*w*	0·1549			*vw*−	0·2829		
w−	0·0495			*m*+	0·1608	0·1608	220	*vvw*	0·2908		
vw	0·0555			*vw*	0·1715			*vvw*	0·2948		
s	0·0602	0·0603	111	*vw*	0·1796			*vvw*	0·3039		
vw	0·0726			*vw*	0·1842			*vvw*	0·3091		
w	0·0805	0·0804	200	*vvw*	0·1960			*w*	0·3216	0·3216	400
vw	0·0849			*vvw*	0·2042						
vvw	0·0972			*vvw*	0·2139						

and hence, *hk*0 and *h*00 when $h = 2n$.

*h*0*l* when $h + l = 2$n

0*kl* and 00*l* when $l = 2$n.

The space groups can thus be *Bmmm*, *Bm*2*m*, *Bmm*2 or B222. Volume considerations suggest four molecules in the cell. (Table 4).

ZrF_4, 3H_2O gives cell parameters from single crystal data of $a = 5{\cdot}94$, $b = 6{\cdot}96$,

Vol. 15 1960

$c = 7{\cdot}55$ Å, $\alpha = 90{\cdot}2$, $\beta = 105{\cdot}0$, $\gamma = 118{\cdot}9°$. A recent report[7] puts them at $a = 5{\cdot}40$, $b = 8{\cdot}05$, $c = 4{\cdot}87$ Å, $\alpha = 105$, $\beta = 90$, $\gamma = 68°$. The $\sin^2\theta$ data have been calculated for both sets of constants and are given in Table 5 for comparison. The agreement between the observed $\sin^2\theta$ values and those calculated from the cell constants determined in the present work suggests that these are substantially correct.

$ZrF,HF,3{\cdot}5–6{\cdot}0H_2O$ gives a diffraction pattern which has not been indexed (Table 6).

TABLE 4.—$ZrF_4,HF,3{\cdot}0H_2O$

I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	*hkl*	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	*hkl*	I_o	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	*hkl*
w+	0·0091	0·0091	010	*w*−	0·0774	0·0772	113	*vw*	0·1340	0·1335	024
w	0·0196	0·0196	101	*vw*	0·0783	0·0783	202	*vw*	0·1368	0·1366	033
w−	0·0243	0·0243	002	*vvw*	0·0817	0·0820	030	*vvw*	0·1457	0·1458	040
w	0·0286	0·0287	111	*w*−	0·0876	0·0874	212	*vvw*	0·1502	0·1501	133
w+	0·0334	0·0334	012	*vvw*	0·0904	0·0904	220	*vvw*	0·1515	0·1510	204
vw	0·0363	0·0364	020	*vvw*	0·0975	0·0971	004	*vvw*	0·1606	0·1602	232
w+	0·0540	0·0540	200	*vvw*	0·1020	0·1016	131	*vw*	0·1657	0·1651	105
w−	0·0563	0·0560	121	*vw*	0·1047	0·1045	123	*vvw*	0·1694	0·1700	042
vvw	0·0609	0·0607	022	*vvw*	0·1062	0·1062	014	*w*	0·1744	0·1743	115
vw	0·0631	0·0631	210	*vvw*	0·1150	0·1147	222				
w	0·0683	0·0681	103	*vw*	0·1277	0·1275	301				

Compound A, the material from the partial drying of $ZrF_4,HF,3{\cdot}0H_2O$, produces diffraction lines which seem to indicate a new compound. They are listed in Table 7.

$ZrOF_2,1{\cdot}3HF,H_2O$ gives a diffraction pattern which has not been indexed, (Table 8).

Phase X, the solid produced when ZrF_4 is boiled in water, gives an unindexed diffraction pattern, (Table 9).

Compound B, produced by the steam hydrolysis of ZrF_4, gives a few diffraction lines which seem to indicate a new compound (Table 10).

The cell constants are also available for the following: ZrF_4,[8] $a = 11{\cdot}71$, $b = 9{\cdot}89$, $c = 7{\cdot}66$ Å, $\beta = 126{\cdot}15°$; space group C^2/c with twelve molecules in the unit cell.

ZrF_4,H_2O,[3] $a = 7{\cdot}72$, $c = 11{\cdot}65$ Å; space group $I4_1md$ or $I\bar{4}2d$ with eight molecules in the unit cell.

ZrO_2 (monoclinic form),[9] $a = 5{\cdot}169$, $b = 5{\cdot}232$, $c = 5{\cdot}341$ Å, $\beta = 99{\cdot}25°$; space group $P2_1/c$.

The powder data obtained here for $ZrOF_2$ were identified from existing results.[10]

Infra-red absorption peaks were obtained in the 3000 cm^{-1} region in the positions shown in Table 11.

The following explanations are given to amplify some of the above evidence.

(i) The products of the hydrolysis of zirconium tetrafluoride with boiling water, phase X, all gave the same diffraction pattern with only a few differences in the

[7] R. L. WELLS, U.S.A.E.C. Report IDO-14455 (1958).
[8] W. H. ZACHARIASEN, *Acta Cryst.* **2**, 388 (1949).
[9] J. D. MCCULLOUGH and K. N. TRUEBLOOD, *Acta Cryst.* **12**, 507 (1959).
[10] A. CHRÉTIEN and B. GAUDREAU, *C.R. Acad. Sci., Paris* **246**, 2266 (1958).

relative intensities of the lines. Analysis showed there was a gradual change in composition from $ZrOF_2,1{\cdot}4HF$ to $ZrOF_2,0{\cdot}1HF,1{\cdot}1H_2O$ which depended on the time of hydrolysis and the proportion of tetrafluoride to water.

TABLE 5.—$ZrF_4,3H_2O$

Present work				Ref. 7		Present work				Ref. 7	
I_o	*hkl*	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	*hkl*	I_o	*hkl*	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	*hkl*
w	001	0·0114	0·0114	0·0116	010	*m*−	$\bar{2}12$	0·0874	0·0871		
s	010	0·0164	0·0164				$\bar{2}01$	0·0880			
s	$\bar{1}10$	0·0205	0·0204				102	0·0895		0·0892	130
s	$0\bar{1}1$	0·0236	0·0236	0·0226	110					0·0904	220
	100	0·0241		0·0240	100					0·0909	$\bar{1}11$
s	$\bar{1}01$	0·0256	0·0254			*w*+	$\bar{1}22$	0·0923	0·0925	0·0922	$\bar{1}31$
m	$\bar{1}11$	0·0262	0·0262	0·0271	001					0·0931	021
				0·0288	$1\bar{1}1$	*w*	200	0·0963	0·0958	0·0958	200
m	011	0·0319	0·0321							0·0959	$\bar{1}20$
w	$1\bar{1}1$	0·0377	0·0375				$\bar{1}03$	0·0973	0·0980	0·0978	$1\bar{2}1$
				0·0444	120		$1\bar{2}2$	0·0985			
	101	0·0454	0·0453	0·0454	$\bar{1}\bar{1}1$	*w*+	$2\bar{1}1$	0·0999	0·0994	0·1003	$0\bar{1}2$
	002	0·0457		0·0456	101					0·1014	$0\bar{3}1$
				0·0462	020	*w*−	$\bar{2}02$	0·1025	0·1025		
				0·0484	$\bar{1}10$		003	0·1028			
				0·0486	011					0·1039	030
m	$\bar{1}20$	0·0497	0·0496			*w*	$2\bar{2}1$	0·1050	0·1047		
vvw	$\bar{1}02$	0·0500	0·0505			*w*	$\bar{1}13$	0·1062	0·1059		
vw	$0\bar{1}2$	0·0537	0·0533	0·0536	$0\bar{2}1$		$0\bar{1}3$	0·1067		0·1075	211
vw	$\bar{1}12$	0·0548	0·0547	0·0541	111					0·1085	002
				0·0566	$\bar{1}01$					0·1088	$\bar{2}2\bar{1}$
vw	$\bar{1}\bar{1}1$	0·0577	0·0573	0·0572	$\bar{1}2\bar{1}$					0·1098	$2\bar{1}1$
	$\bar{1}21$	0·0596				*vvw*	$\bar{1}30$	0·1116	0·1117	0·1119	201
w+	110	0·0603	0·0603	0·0601	$1\bar{1}1$					0·1152	$0\bar{2}2$
vw	$1\bar{2}1$	0·0627	0·0624			*m*	$1\bar{3}1$	0·1204	0·1197		
vvw	020	0·0654	0·0654			*vvw*	$\bar{1}\bar{1}3$	0·1210	0·1217	0·1214	102
m−	$0\bar{2}1$	0·0685	0·0683				$\bar{1}2\bar{1}$	0·1225		0·1224	230 and $\bar{1}\bar{1}2$
	$\bar{2}11$	0·0687									
m	012	0·0704	0·0705								
	$\bar{2}10$	0·0729				*vvw*	$\bar{2}30$	0·1241	0·1241	0·1244	$\bar{1}22$
m−	$1\bar{1}2$	0·0776	0·0773			*vvw*	$\bar{1}31$	0·1256	0·1259	0·1261	$1\bar{1}2$
	$\bar{1}\bar{1}2$	0·0780								0·1263	221
m	$\bar{2}21$	0·0821	0·0821	0·0815	210	*vw*	201	0·1274	0·1271		
	$\bar{2}20$	0·0821				*w*+	$\bar{2}31$	0·1283	0·1283		
w−	021	0·0852	0·0852	0·0857	121		$\bar{2}13$	0·1289			
	111	0·0858									

(ii) Material of the composition $ZrOF_2,2H_2O$ previously reported[11] could not be prepared but a compound $ZrOF_2,1{\cdot}3HF,H_2O$ was obtained by hydrolysing ZrF_4,H_2O with water at room temperature.

(iii) The exact conditions leading to the preparation of $ZrF_4,2HF,0{\cdot}7H_2O$ and $ZrF_4,HF,1{\cdot}5H_2O$ are not known. The former is stable at room temperature and is

[11] I. V. TANANAEV, N. S. NIKOLAEV and YU. A. BUSLAEV, *Zh. Neorg. Khim.* **1**, 274, (1956).

Vol. 15 1960

TABLE 6.—$ZrF_4,HF,3{\cdot}5\text{–}6{\cdot}0H_2O$

I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.
s	0·0078	*s*	0·0565	*vvw*	0·0895	*w*−	0·1327
vw	0·0107	*w*	0·0590	*vvw*	0·0953	*w*	0·1407
m	0·0199	*vw*	0·0606	*vvw*	0·0998	*w*+	0·1484
m	0·0238	*m*	0·0660	*vvw*	0·1033	*vw*	0·1526
s	0·0249	*m*	0·0697	*w*	0·1051	*w*	0·1581
m+	0·0313	*w*−	0·0706	*vw*	0·1089	*m*	0·1620
vvw	0·0355	*w*	0·0722	*w*	0·1189	*vvw*	0·1682
vvw	0·0395	*m*	0·0776	*m*−	0·1233	*w*−	0·1696
m	0·0406	*w*−	0·0796	*w*	0·1250	*w*	0·1753
w+	0·0434	*w*	0·0855	*w*	0·1289	*w*	0·1789

TABLE 7.—COMPOUND A

I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.
s	0·0155	*w*+	0·0404	*vvw*	0·0749	*vvw*	0·1561
s	0·0188	*s*	0·0539	*vw*	0·1127	*vvw*	0·1586
w+	0·0216	*vw*	0·0608	*vw*+	0·1401	*vw*	0·1752
vw	0·0243	*vvw*	0·0620	*vw*	0·1485		

TABLE 8.—$ZrOF_2,1{\cdot}3HF,H_2O$

I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.
m+	0·0088	*w*	0·0353	*vw*+	0·0693	*vvw*	0·1223
w	0·0193	*vw*	0·0393	*vw*	0·0706	*w*	0·1260
w	0·0205	*vvw*	0·0453	*vvw*	0·0733	*vw*	0·1308
w+	0·0214	*vw*	0·0498	*vvw*	0·0756	*w*−	0·1351
w+	0·0238	*vw*	0·0534	*vvw*	0·0773	*vvw*	0·1390
vvw	0·0253	*s*	0·0557	*m*	0·0794	*vw*	0·1413
vvw	0·0263	*vvw*	0·0574	*vw*	0·0972	*vvw*	0·1464
vw	0·0281	*vvw*	0·0592	*vvw*	0·1024	*w*	0·1511
vvw	0·0310	*vvw*	0·0621	*vvw*	0·1035	*vvw*	0·1578
w+	0·0326	*vw*	0·0669	*vvw*	0·1064		

TABLE 9.—PHASE X

I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.
s	0·0125	*s*	0·0392	*s*	0·0557	*vvw*	0·1007
vvw	0·0144	*vw*	0·0411	*vw*	0·0575	*vvw*	0·1199
vw	0·0163	*vw*	0·0416	*vvw*	0·0691	*vw*	0·1307
w−	0·0178	*vw*	0·0426	*vvw*	0·0707	*vvw*	0·1364
vvw	0·0197	*vw*	0·0446	*vvw*	0·0806	*w*−	0·1384
vvw	0·0235	*w*−	0·0496	*vvw*	0·0846	*w*	0·1575
vw+	0·0310	*s*	0·0517	*vvw*	0·0890	*w*	0·1698

possibly identical with $ZrF_4,2HF,H_2O$ which decomposes at 112°C.[11] These compounds may all be members of a class which includes $H_3Zr_2F_{11},5H_2O$,[12] also previously reported.

(iv) There is some evidence of a compound with a composition between ZrF_4,H_2O and $ZrOF_2$ in the form of unidentifiable X-ray diffraction lines which were observed when the monohydrate was heated in air at 250°C. Prolonged heating at this temperature gave material showing only the $ZrOF_2$ pattern. The lines in question may have been due to $ZrOF_2,HF$ which had been previously found during the degradation of

TABLE 10.—COMPOUND B

I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.	I_o	$\sin^2\theta$ obs.
vw	0·0101	*vw*	0·0414	*vw*	0·0781	*vw*	0·1503
m	0·0252	*m*−	0·0525	*m*−	0·0794	*vw*	0·1541
m	0·0288	*vw*	0·0626	*vvw*	0·1157	*vw*	0·1600
m+	0·0374	*vw*	0·0686	*vw*	0·1343	*vw*	0·1749

ZrF_4,H_2O.[11] There was similar evidence for the two compounds A and B but as they were always minor constituents they could not be studied further.

The analytical results for the compounds identified are given below.

$ZrF_4,2HF,0{\cdot}7H_2O$. Found Zr = 41·0, F = 52·1. Calc. Zr = 41·5, F = 51·9%

$ZrF_4,HF,1{\cdot}5H_2O$ Found Zr = 42·7, F = 43·8. Calc. Zr = 42·6, F = 44·3%

$ZrF_4,HF,3{\cdot}0H_2O$ Found Zr = 37·7, F = 39·3. Calc. Zr = 37·8, F = 39·4%

$ZrF_4,3H_2O$ Found Zr = 41·7, F = 34·9. Calc. Zr = 41·2, F = 34·4%

$ZrF_4,HF,3{\cdot}5$–$6{\cdot}0H_2O$ The lower limit of composition was established as $ZrF_4,HF,3{\cdot}5H_2O$ (Found Zr = 36·3, F = 37·8. Calc. Zr = 36·5, F = 38·0%) but the upper limit is unknown. The Zr: F ratio was always found to be nearly 1:5 but the mass difference, ascribed to water, may have been due to surface moisture as the compound was unstable to even gentle drying. That this was a new compound was inferred from the X-ray evidence and it was designated $ZrF_4,HF,3{\cdot}5$–$6{\cdot}0H_2O$ to accord with the analytical results.

$ZrOF_2,1{\cdot}3HF,H_2O$ Found Zr = 48·3, F = 33·6. Calc. Zr = 48·2, F = 33·1%. Without a more complete analysis the distinction between the oxygen in the $ZrOF_2$ group and in the water molecule cannot be made, but the compound has been written as the oxyfluoride as it is probably a hydrolysis product of ZrF_4,H_2O.

ZrF_4 Found Zr = 54·7, F = 44·9. Calc. Zr = 54·6, F = 45·5%.

ZrF_4,H_2O Found Zr = 49·3, F = 40·4. Calc. Zr = 49·3, F = 41·0%.

$ZrOF_2$ Found Zr = 61·3, F = 24·7. Calc. Zr = 62·8, F = 26·2%.

The mass difference brings the composition to $ZrO_{1\cdot3}F_2$ but the diffraction pattern showed the bulk of the material to be $ZrOF_2$. The presence of undecomposed ZrF_4, H_2O or of ZrO_2 possibly accounts for the analytical figures.

[11] O. RUFF and G. LAUSCHKE, *Z. Anorg. Chem.* **97**, 110 (1916).

Vol. 15 1960

DISCUSSION

The hydrolysis of zirconium tetrafluoride leads to a complex system of compounds and mixtures and even where the compounds could be isolated an elucidation of their structures has proved difficult. Attempts to use X-ray powder data for deriving the structures of ZrF_4,H_2O, $ZrF_4,HF,3H_2O$, and $ZrF,HF,0{\cdot}7H_2O$ were unsuccessful because of the large unit cells and the choice of space groups. Single crystal data have been collected for $ZrF_4,3H_2O$ and a full structural analysis of this hydrate has begun. Meanwhile, in the absence of this specific information a tentative scheme is advanced to account for the results described above.

(i) *Compounds* ZrF_4,xHF,yH_2O

Both ZrF_4,H_2O and $ZrF_4,3H_2O$ can be prepared by dissolving zirconium tetrafluoride in aqueous hydrofluoric acid or by allowing it to react with steam, but in each instance the lowest hydrate produced is the monohydrate. In this, zirconium differs from thorium tetrafluoride where hydrates with a fractional water content can be prepared.[2] If it be assumed that water first acts by making a direct attachment of oxygen to zirconium, the formation of the monohydrate, better designated perhaps $ZrOF_2,2HF$ than ZrF_4,H_2O, is explained. The action of steam on the tetrafluoride powder, to produce the hydrates, suggests the breaking of two Zr—F—Zr linkages per zirconium atom to give Zr—O and F—Zr. This maintains the eightfold co-ordination of zirconium found in the tetrafluoride but destroys the complete three-dimensional network of the latter. This "loosening" of the structure and its consequent rearrangement to the tetragonal monohydrate, with cell dimensions of $a = 7{\cdot}72$, $c = 11{\cdot}65$ Å not dissimilar from the [*c*] and [*a*] dimensions of the monoclinic tetrafluoride ($c = 7{\cdot}66$, $a = 11{\cdot}71$ Å) accords with a fall in the calculated density from 4·65 g/cm³ to 3·54 g/cm³.

Preliminary results from the structural analysis of the trihydrate suggest that the process of bond-breaking extends to four more Zr-F-Zr linkages per zirconium atom, leaving dimers of the form O_3F_3—Zr^F_FZr—F_3O_3. These still have the eightfold co-ordination arrangement of two superimposed distorted tetrahedra around each metal atom already found in ZrF_4 and K_2ZrF_6.[13] The approximate atomic positions suggest that the dimers are held together by hydrogen bonds to form continuous sheets separated by approximately 4 Å and held together by van der Waal's forces. The formation of $ZrF_4,HF,3{\cdot}0H_2O$ and $ZrF_4,HF,3{\cdot}5$–$6{\cdot}0H_2O$ arises from the insertion of water and hydrofluoric acid molecules between the sheets. As a consequence the calculated density of $ZrF_4,HF,3{\cdot}0H_2O$ is 3·02 g/cm³, definitely higher than that calculated for the parent $ZrF_4,3H_2O$ which is 2·81 g/cm³. Further, if the lattice constants of $ZrF_4,HF,3{\cdot}0H_2O$ be expressed in terms of a monoclinic cell with $a = 5{\cdot}97$, $b = 8{\cdot}07$, $c = 6{\cdot}63$ Å, $\beta = 124°$, the [*a*] axis proves to be almost identical with one of the trihydrate axes ($a = 5{\cdot}94$ Å) which lies in the plane of the sheets. It is likely that $ZrF_4,HF,3{\cdot}5$–$6{\cdot}0H_2O$ and the compound A arise in the same way.

[13] H. Bode and G. Teufer, *Acta Cryst.* **9**, 929 (1956).

Thus the readiness with which all the compounds degrade to the trihydrate is easily understood, and the formation of $ZrOF_2$ on vigorous dehydration would be expected from the initial attachment of oxygen to zirconium.

It is interesting to compare the hydrates described with those of thorium tetrafluoride. Of the latter, many have a fractional water content, for instance $ThF_4,0{\cdot}25H_2O$, $ThF_4,0{\cdot}35H_2O$ and $ThF_4,0{\cdot}9H_2O$[1,2] one at least of which arises from the insertion of water molecules into voids in the thorium tetrafluoride lattice. Furthermore, tetrafluoride can be recovered from all the hydrates by vigorous drying.

TABLE 11

$ZrF_4,3H_2O$ (cm^{-1})	$ZrF_4,HF,1{\cdot}5H_2O$ (cm^{-1})
3510	3500
3370	3370
3225	3240
3130	3130

The place of $ZrF_4,2HF,0{\cdot}7H_2O$ and $ZrF_4,HF,1{\cdot}5H_2O$ in the above scheme is unknown. The former has an hexagonal cell containing three molecules. About the latter more may be said. It shows a strong pseudo face-centred cubic diffraction pattern with 1·3–1·4 molecules per cubic cell. The cube edge of 5·43 Å suggests that the pseudo structure may be based on the fluorite cell with a random distribution of fluoride ions in the anion positions and zirconium ions, and perhaps water molecules, in the cation positions. Some ordering of this arrangement should then give the superlattice lines observed. This compound has an infra-red absorption spectrum in the 1500–4000 cm^{-1} region very similar to that of $ZrF_4,3H_2O$. Both show a broad band at approximately 3000 cm^{-1} (Table 11), presumably due to O—H and F—H stretching vibrations, which illustrates the complexity of the hydrogen bonding in these compounds and indicates a similarity in their nature.

(ii) *Hydrolysis compounds* $ZrOF_2,xHF,yH_2O$

The processes occurring during the hydrolysis of zirconium tetrafluoride by water and steam are even less clear. If one again assumes that zirconium maintains an eightfold co-ordination number, then the replacement of fluorine by hydroxyl ions could give a large number of compounds, particularly should the elimination, or absorption, of water also occur. The solid hydrolysis products found either after boiling the tetrafluoride in water, or on passing steam over it at 200°C, are probably such compounds. The formation of $ZrF_4,HF,3{\cdot}0H_2O$ at 200°C is probably due to the previous formation of $ZrF_4,3H_2O$ and its absorption of hydrofluoric acid released by hydrolysis.

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Vol. 15 1960

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STRUCTURAL PRINCIPLES OF THE HYDRATED POLYBORATES

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Abstract—The principles governing the structures of the stable hydrated polyborates are postulated on the basis of an analysis of the known configurations. The fundamental unit of the polyanionic structures is a trimeric ring containing both trigonal and tetrahedral boron atoms. The formation of the tetramer, pentamers, etc. and long-chain polyanions results from the fusion of two or more rings at the tetrahedral boron atoms, or from dehydration.

THE elucidation of the structures of the hydrated polyborates has been difficult due to the occurrence of boron in trigonal and tetrahedral co-ordination; to the rapid interconversion of the various structures; and to the anomalies existing between solid and solution phenomena. For example, a polyborate anion incorporating both trigonal and tetrahedral borate groups has been determined to exist in borax. The properties of the aqueous solution of borax are analogous to those of a mixture of boric acid and sodium borate. On evaporation, borax is recrystallized.

The purpose of this paper is to present arguments pertaining to the bonding in the stable hydrated borate compounds. A set of five postulates governing the principles of bonding in the polyanions has been suggested by analysis of structural configurations obtained from X-ray and NMR studies. A rational is provided of the more common types of hydrated borate compounds and minerals.

The postulates are stated in Section A; a discussion of the postulates follows in Section B. A review of the various structures in light of the postulates is presented in Section C.

A. POSTULATES

(i) In the solid hydrated borates, boron exists in three and four-fold co-ordination by oxygen. The ratio of tetrahedral boron to total boron is equivalent to the ratio of cation charge to total boron.
(ii) The basic structure of the polyborates is a six-atom ring with alternate boron and oxygen atoms.
(iii) The stability of the ring is dependent on the presence of one or two tetrahedral boron atoms.
(iv) Other discrete anions may be formed by the fusion of two rings at a tetrahedral boron atom.
(v) Long chain polyanions may be formed from the rings by repeated dehydration.

B. DISCUSSION OF POSTULATES

(i) *In the solid hydrated borates, the ratio of tetrahedral boron to total boron is equivalent to the ratio of cation charge to total boron*

This postulate may be phrased in several ways. One alternative is to state that

boron in the borates acts as a Lewis acid rather than a Brönsted acid. It has been demonstrated that the borate ion[1] and related ions such as phenylboronate[2] and peroxyborate[3] are tetrahedral, hence the reaction

$$H_2BO_3^- + H_2O \rightleftharpoons B(OH)_4^-$$

has a negative free energy (proceeds spontaneously to the right).

Since the total negative charge on the polyborate anion is equal to the cation charge, it follows that one tetrahedral boron atom will prevail for each positive charge. Known crystalline examples are cited in Table 1. In further support of this argument,

TABLE 1

Compound	Formula	Cation charge	Number boron atoms	Ratio B_{tet}/B_{total}
Teepleite[5,6]	$NaBO_2 \cdot NaCl \cdot 2H_2O$	1*	1	1/1
Bandylite[6,7]	$CuB_2O_4 \cdot CuCl_2 \cdot 4H_2O$	2*	2	2/2
Sodium peroxyborate[3]	$NaBO_2 \cdot 4H_2O$	1	1	1/1
Pinnoite[8]	$MgB_2O_4 \cdot 3H_2O$	2	2	2/2
Colemanite[9]	$Ca_2B_6O_{11} \cdot 5H_2O$	4	6	2/3
Meyerhofferite[10]	$Ca_2B_6O_{11} \cdot 7H_2O$	4	6	2/3
Inyoite[11]	$Ca_2B_6O_{11} \cdot 13H_2O$	4	6	2/3
Kernite[3,12]	$Na_2B_4O_7 \cdot 4H_2O$	2	4	2/4
Tincalconite[3]	$Na_2B_4O_7 \cdot 5H_2O$	2	4	2/4
Borax[3,13]	$Na_2B_4O_7 \cdot 10H_2O$	2	4	2/4
Potassium pentaborate[3,14]	$KB_5O_8 \cdot 4H_2O$	1	5	1/5

* This is the net charge which must reside on the polyborate ion since half of the cation charge is balanced by the chloride ion(s).

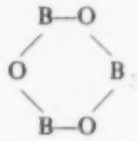
the amount of tetrahedral boron in the alkali-borate glasses has been directly correlated by NMR analysis[4] of the B″ resonance with the amount of alkali oxide present (i.e. below the saturation limit).

[1] J. O. EDWARDS, G. C. MORRISON, V. F. ROSS and J. W. SCHULTZ, *J. Amer. Chem. Soc.* **77**, 266 (1955).
[2] J. LORAND and J. O. EDWARDS, *J. Org. Chem.* **24**, 769 (1959).
[3] P. J. BRAY, J. O. EDWARDS, J. O'KEEFE and V. ROSS, Abstracts of the Annual Meeting of the American Crystallographic Association. p. 29 (1959).
[4] A. H. SILVER, Thesis, Rensselaer Polytechnic Institute (1958); A. H. SILVER and P. J. BRAY, *J. Chem. Phys.* **29**, 984 (1958).
[5] M. FORNASERI, *Period. Min.* **18**, 103 (1949).
[6] V. ROSS and J. O. EDWARDS, *Amer. Min.* **44**, 875 (1959).
[7] R. L. COLLIN, *Acta Cryst.* **4**, 204 (1951).
[8] F. PATON and S. G. MACDONALD, *Acta Cryst.* **10**, 653 (1947).
[9] C. L. CHRIST, J. R. CLARK and H. T. EVANS, JR. *Acta Cryst.* **7**, 453 (1954).
[10] C. L. CHRIST and J. R. CLARK, *Acta Cryst.* **9**, 830 (1956).
[11] J. R. CLARK, *Acta Cryst.* **12**, 162 (1959).
[12] V. ROSS and J. O. EDWARDS, *Acta Cryst.* **12**, 258 (1959).
[13] N. MORIMOTO, *Min. J. Japan* **2**, 1 (1956).
[14] W. H. ZACHARIASEN, *Zh. Krist.* **98**, 266 (1937).

Vol. 15 1960

(ii) *The basic structure of the polyborates is a six-atom ring with alternate boron and oxygen atoms*

All structures illustrated will have the configuration

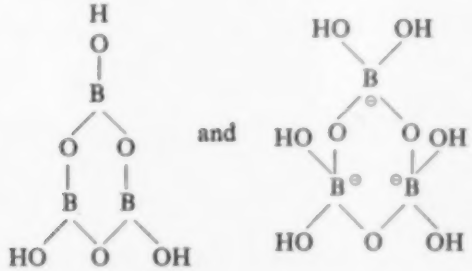


as an integral part of the polymer. The predominant polymeric species in dilute borate solutions is a trimer, consistent with a ring structure as discussed by INGRI *et al.*[15] The formation of linear polymers would strongly imply the presence of dimers and this has not been found to be the case. It is thus inferred that the trimer in the form of a six-atom anionic ring, occurring in both aqueous solution and in the crystalline polyborates, is characterised by unusual stability.

(iii) *The stability of the ring is dependent on the presence of one or two tetrahedral boron atoms*

In systems in which water has a reasonable activity, certain types of rings (although comprised of six-atoms) are unstable. The metaborate ion $(B_3O_6)^{3-}$ will hydrate very rapidly and lose the ring structure. A similar situation is true for the metaboric acid ring $B_3O_3(OH)_3$ which spontaneously alters to $B(OH)_3$. Furthermore, no evidence for a neutral polymer $(HBO_2)_x$ has been found in solutions of boric acid.[16] Nor has any evidence been encountered for polyanions in which each boron atom is negatively charged[1,17] i.e. in borate ion solutions.

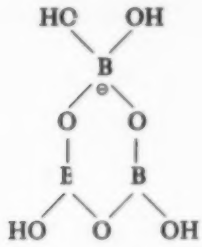
It is therefore likely that the two structures:



are unstable relative to their monomeric forms, trigonal $B(OH)_3$ and tetrahedral $B(OH)_4^-$, respectively.

There is, on the other hand, considerable evidence for polymer formation when *both* boric acid and borate ion are present in solution.[15,18,19,20,21,22] Rings of the type

[15] N. INGRI, G. LAGERSTROM, M. FRYDMAN and L. G. SILLEN, *Acta Chem. Scand.* **11**, 1034 (1957).
[16] H. MENZEL, *Z. Anorg. Chem.* **164**, 1 (1927).
[17] H. MENZEL and H. SCHULTZ, *Z. Anorg. Chem.* **251**, 167 (1943).
[18] B. B. OWEN, *J. Amer. Chem. Soc.* **56**, 1695 (1934).
[19] J. E. THYGESEN, *Z. Anorg. Chem.* **237**, 101 (1938).
[20] D. STETTEN, *Analyt. Chem.* **23**, 1177 (1951).
[21] J. O. EDWARDS, *J. Amer. Chem. Soc.* **75**, 6151 (1953).
[22] P. J. ANTIKAINEN, *Suomen Kem.* B **30**, 74 (1957).



appear to be highly stable. (Refer to Structure I.) The equilibrium constant for the reaction:

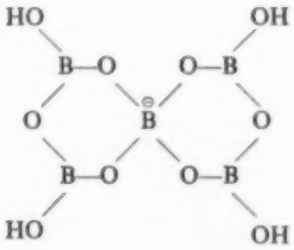
$$2H_3BO_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O$$

is 110, of respectable magnitude.[21]

The ring system with two tetrahedral and one trigonal boron atom is also stable. (Refer to Structure II.)

(iv) *Other discrete anions may be formed by the fusion of two rings at a tetrahedral boron atom*

There are several polyborate minerals and compounds which consist of discrete anions, yet formula-wise do not contain $B_3O_3(OH)_4^-$ or $B_3O_3(OH)_5^{2-}$ groups. These anions are postulated to be derived from the basic ring elements linked by shared tetrahedral boron atoms. For example, the pentaborate ion has the structure[14]

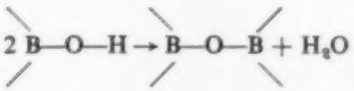


in which one tetrahedral boron atom is shared in common by two perpendicular rings. (Refer to Structures III, IV and V.)

A related type of fusion is found in the polyborate anion of borax in which two six-atom rings are joined by two common tetrahedral boron atoms.[13] (Refer to Structure VI.)

(v) *Long chain polyanions may be formed from the rings by repeated dehydration*

Long chains are known in some hydrated polyborate minerals. Two means of formation of such chains from the basic trimeric ring structures are postulated. The first is by repeated dehydration of the type

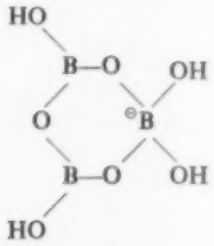


Vol. 15 1960

using either trigonal or tetrahedral borate groups. This manner of polymerization has been proposed by CHRIST[23,24] in application to the polyborate chain structures. An alternative means entails the repeated fusion of rings comprised of two tetrahedral and one trigonal boron atoms. Examples of the various systems are included in the discussion of structures I, II and VI and VII.

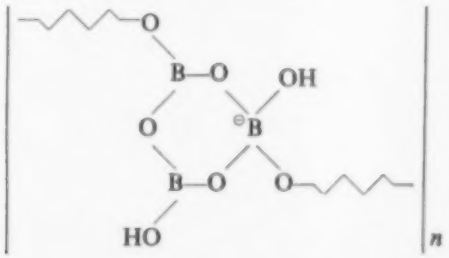
C. DISCUSSION OF STRUCTURES

1. The trimeric-ring polyanion



is the most satisfactory explanation for the predominant polymer species in aqueous solution at concentrations of boric acid greater than 0·025 M.[15] It is postulated also to be the structural group $B_3O_3(OH)_4^-$ in the stable compounds: $LiB_3O_5 \cdot 3H_2O$, $CaB_6O_{10} \cdot 4$, 8, 12 H_2O and $MgB_6O_{10} \cdot 7$–8 H_2O.

The existence of a long chain polymer shown below, with successive dehydration linkages to give the formula $B_3O_4(OH)_2^-$, is equally probable and could occur in the lowest hydrate of each system, for example, the dihydrate $SrB_6O_{10} \cdot 2H_2O$ (veatchite)[25]

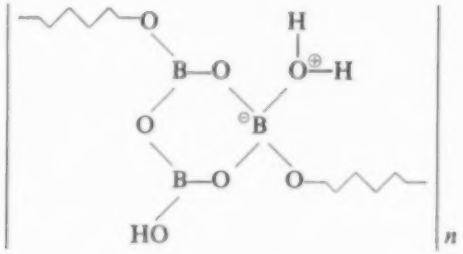


A similar chain unit may be deduced from the preliminary structural description of monoclinic meta-boric acid, HBO_2-II, provided by ZACHARIASEN[26]. The formation of a chain structure from the ring form of orthorhombic metaboric acid,[27] HBO_2-I would presumably involve the stoichiometric reaction

$$nB_3O_3(OH)_3 \rightarrow B_3O_4(OH)_n + nH_2O$$

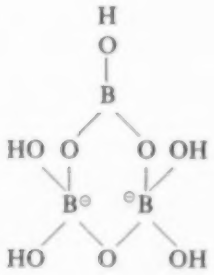
[23] C. L. CHRIST, Abstracts of the Annual Meeting of the American Geological Society, p. 38 (1957).
[24] P. J. BRAY, J. O. EDWARDS, J. O'KEEFE and V. ROSS, Abstracts of the Annual Meeting of the American Crystallographic Association, p. 28 (1959).
[25] J. R. CLARK, M. MROSE, C. L. CHRIST, S. BLOCK and G. PERLOFF, *Bull. Geol. Soc. Amer.* **69**, 1547 (1958).
[26] W. H. ZACHARIASEN, *Acta Cryst.* **5**, 68 (1952).
[27] H. TAZAKI, *J. Sci. Hiroshima Univ.* A **10**, 55 (1940).

The water and the ring in the chain may then recombine by co-ordinate-covalent bonding to give a tetrahedral boron atom with a formal negative charge and an oxygen atom with a formal positive charge as in the structure



This unique structure may be explained on the basis of the postulates as follows: the instability resulting from charge separation is counter-balanced by the added stability of a tetrahedral boron atom in the six-membered ring.

II. The fundamental ring-trimeric polyanion with two tetrahedral boron atoms



is also thought to occur in aqueous solution at high concentrations of boric acid and borate ion.[15] It is the structural element $B_3O_3(OH)_5^{2-}$ in the minerals meyerhoffe-rite,[10] $Ca_2B_6O_{11}\cdot 7H_2O$ and inyoite, $Ca_2B_6O_{11}\cdot 13H_2O$[11]. The polymerization of the latter rings to form the chain structure of colemanite[9] which contains the polyanion unit $B_3O_4(OH)_3^{2-}$ is accomplished by splitting out one mole of water.[23] The NMR analyses of colemanite by HOLUJ and PETCH[28] confirm the existence of one trigonal and two tetrahedral boron atoms in the polyanionic unit.

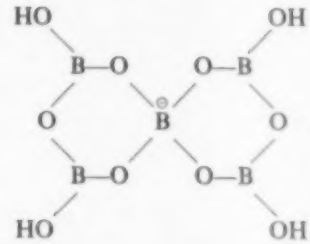
The hydrated triborates of calcium and magnesium are known to be highly stable and common mineral occurrences. The mineral inderite, $Mg_2B_6O_{11}\cdot 5H_2O$, according to PETCH[29] gives indication of having the same structural configuration on the basis of NMR analysis, i.e. a polyanion comprised of one trigonal and two tetrahedral boron atoms. It appears that the double salts of calcium and magnesium triborate (hydroboracite and inderborite) may also be analogous.

The trimers I and II appear to be favoured in the presence of cations of smaller size and relatively large ionic potential i.e. Ca, Mg, Sr and Li, discussed in the following sections.

[28] F. HOLUJ and H. E. PETCH, *Canad. J. Phys.* **36**, 145 (1958).
[29] H. E. PETCH. Private communication.

Vol. 15 1960

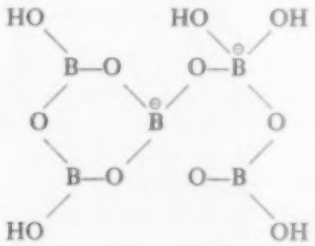
III. Two perpendicular trimeric rings are fused by a common tetrahedral boron atom in the pentamer



of the stable natural and synthetic pentaborates. The synthetic phases include potassium pentaborate, $KB_5O_8{\cdot}4H_2O$[14], $NH_4B_5O_8{\cdot}4H_2O$ (which is probably the mineral larderellite) and several quaternary ammonium pentaborates.[30] The stability of the pentaborate is evident from the fact that one additional mole of boric acid appears to be occluded in the structures of the latter compounds precluding the formation of a true hexaborate. In the systems K_2O–B_2O_3–H_2O and $(NH_4)_2O$–B_2O_3–H_2O, there is a wide range of stability for the pentaborate. The structural arrangement of the anion permits the easy incorporation of large cations of relatively low ionic potential. In this respect it is not surprising to find that the field of stability of the corresponding sodium pentaborate is quite narrow. The existence of chemically analogous cesium and rubidium pentaborates has been indicated by ROLLET and ANDRES[31].

IV. The pentaborate complex is apparently quite stable and may be modified by the addition of negative charges to the ring system and the formation of tetrahedral boron atoms. These modifications would explain a large family of stable pentaborate minerals and compounds.

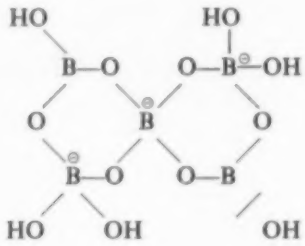
The polyanion $B_5O_6(OH)_5^{2-}$, which has also been proposed by CHRIST[24], is formed by the addition of a second negative charge on the pentamer and results in the formation of an additional tetrahedral boron atom in the ring system.



This structural unit may exist in the compound described by CARPENI[32] having the formula $K_2HB_5O_9{\cdot}H_2O$ and in AUGER's sodium and potassium borates, $Na_4B_{10}O_{17}{\cdot}5H_2O$ and $K_4B_{10}O_{17}{\cdot}5H_2O$, respectively[33] and the mineral, ezcurrite, $Na_4B_{10}O_{17}{\cdot}7H_2O$.[34]

[30] R. C. PETERSON, M. FINKELSTEIN and S. D. ROSS, *J. Amer. Chem. Soc.* **81**, 3264 (1959).
[31] A. P. ROLLET and L. ANDRES, *C. R. Acad. Sci., Paris* **191**, 567 (1930).
[32] G. CARPENI, *C. R. Acad. Sci., Paris* **239**, 1500 (1954).
[33] V. AUGER, *C. R. Acad. Sci., Paris* **180**, 1602 (1925).
[34] S MUESSIG and R. D. ALLEN, *Econ. Geol.* **52**, 426 (1957).

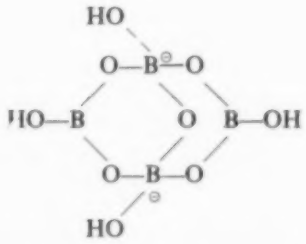
V. The pentaborate ring system containing three negatively charged boron atoms in tetrahedral co-ordination is postulated as



From preliminary NMR studies[3] of the boron atom coordination, it is probable that the polyanion $B_5O_6(OH)_6^{3-}$ is found in the double salts $NaCaB_5O_9 \cdot 8H_2O$ (ulexite) and $NaCaB_5O_9 \cdot 5H_2O$ (probertite).

In addition to the polyanions IV and V, above, CHRIST[24] has proposed the polyanion $B_5O_6(OH)_7^{4-}$. Thus far, there has been no evidence to demonstrate the stability of a trimeric ring with three component tetrahedral boron atoms. The chemical formula $Ca_4B_{10}O_{19} \cdot 7H_2O$ of the mineral priceite, however, appears to be an exception to the postulates, but this phase has not been well-defined and appears to be unstable.

VI. The structural tetramer of borax, $Na_2B_4O_7 \cdot 10H_2O$ may be analyzed as a pair of trimeric rings fused by two shared tetrahedral boron atoms and bent about a common oxygen atom



This polyanion is inferred from NMR analysis[3] to be present also in the structure of sodium tetraborate pentahydrate (tincalconite). The close structural relationship of tincalconite and borax is evident also from the highly reversible conversion of the phases at moderately low temperature (about 55°C) and atmospheric pressure. On the other hand, the dehydration of borax to form the tetrahydrate of sodium tetraborate (kernite) is more difficult, involving polymerization of the polyanions into chains.[35] On the basis of NMR and X-ray studies,[12] the structure of kernite has been proposed to contain chains of the same polyanion having the formula: $\{B_4O_6(OH)_2^{2-}\}_n$. The existence of stable hydrated ammonium and potassium tetraborate species have also been cited in the literature.[36]

VII. The basic postulates suggest the existence of higher-order polyborate structures. The fusion of an additional ring or rings would yield heptamers, nonamers

[35] C. L. CHRIST and R. M. GARRELS, *Amer. J. Sci.* **257**, 516 (1959).
[36] P. H. KEMP, *The Chemistry of the Borates* pp. 45, 65. Borax Consol. Ltd., London (1956).

Vol. 15 1960

and larger odd-numbered borates, with concurrent limitations on the formal negative charge on the polyanion. Included may be such phases as $KMg_2B_{11}O_{19}\cdot 9$ or 19 H_2O (kaliborite) which, indeed, have been reported,[37] but further experimental study of these systems is essential before serious discussion is warranted.

In the case of the repeated fusion of trimeric rings to form a very long-chain polymer, the final product would have the formula $MB_2O_3(OH)$ with the possibility of water of crystallization.

Acknowledgement—We are grateful to the U.S. Atomic Energy Commission for continued support.

[37] C. Palache, H. Berman and C. Frondel, *Dana's System of Mineralogy* Vol. 2, p. 321. John Wiley, New York (1950).

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 338 to 351. Pergamon Press Ltd.

THE CRYSTAL STRUCTURE OF CESIUM BIURANYL TRISULPHATE, $Cs_2(UO_2)_2(SO_4)_3$*

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(*Received* 1 *December* 1959)

Abstract—The crystal structure of the new compound $Cs_2(UO_2)_2(SO_4)_3$ has been determined by X-ray diffraction methods. The compound is tetragonal, space group $P\bar{4}2_1m$ (D_{2d}^3), with $a = 9{\cdot}62 \pm 0{\cdot}02$, $c = 8{\cdot}13 \pm 0{\cdot}01$ Å, and $Z = 2$; s.g. (calc.) $= 4{\cdot}80 \pm 0{\cdot}03$, s.g. (obs.) $= 4{\cdot}74 \pm 0{\cdot}05$. The compound forms plates parallel to (001) bounded by the form (110). Intensity data were obtained from Buerger precession photographs of the (*hk*0) and (0*kl*) reciprocal lattice nets. No corrections for absorption were made. The co-ordinates of the U and Cs atoms were obtained by interpretation of the Patterson projections normal to (001) and (100) and a plausible structure was derived from electron density projections. The final parameters of the structure were determined from subtraction electron density maps, least squares analysis of the structure factors, and spatial considerations.

The compound has a layer structure consisting of $[(UO_2)_2(SO_4)_3]_n^{2n-}$ sheets parallel to (001), tied together by cesium ions. The UO_2^{2+} group is co-ordinated by five sulphate oxygens which form a nearly plane pentagon approximately normal to the uranyl axis. The Cs_2 atom is co-ordinated by twelve oxygen atoms and the Cs_1 atom by eight oxygen atoms.

X-ray and optical data are also given for the compound $Rb_2UO_2(SO_4)_2{\cdot}2H_2O$.

Vol. 15 1960

The complex ions formed by hexavalent uranium in aqueous solution are considered to play an important role in the transport and deposition of uranium in nature, as well as in the weathering of uraniferous ore bodies.[1] The present investigation, of which this paper is a part, was undertaken to determine the crystal structures of certain uranyl complex compounds containing various anions, in order to understand more fully the structural nature of the complex species involved in the transport of uranium in ground waters.

The reaction of uranyl ion with sulphate ions, in acid solutions where hydrolysis is negligible, has been investigated by Ahrland[2]. He found by electrometric and extinctiometric methods that mononuclear complexes with the following association constants were formed:

$$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4 \qquad K_1 = 50 \pm 10$$
$$UO_2^{2+} + 2SO_4^{2-} \rightarrow UO_2(SO_4)_2^{2-} \qquad K_2 = 350 \pm 150$$
$$UO_2^{2+} + 3SO_4^{2-} \rightarrow UO_2(SO_4)_3^{4-} \qquad K_3 = 2500 \pm 1000$$

Further association constants could not be measured. Such studies give no direct

* Publication authorized by the Director, U.S. Geological Survey. The work described is based on a thesis submitted by M. Ross in partial fulfillment of the requirements for the degree of Master of Science, University of Maryland, College Park, Maryland.

[1] R. M. Garrels and C. L. Christ, *U.S. Geol. Survey Prof. Paper* 320, p. 81 (1959).
[2] S. Ahrland, *Acta Chem. Scand.* 5, 1151 (1951).

information concerning the structures of the complexes formed, nor of the part played by water in their formation.

From aqueous solutions containing such uranyl sulphate complexes, the following compounds have been crystallized by COLANI[3,4]:

I. $UO_2SO_4 \cdot 3H_2O$
II. $H_2UO_2(SO_4)_2 \cdot 5H_2O$
III. $(NH_4)_2(UO_2)_2(SO_4)_3 \cdot 5H_2O$
IV. $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$
V. $Na_2UO_2(SO_4)_2 \cdot 3H_2O$
VI. $Na_4UO_2(SO_4)_3 \cdot 3H_2O$
VII. $K_2(UO_2)_2(SO_4)_3 \cdot 5H_2O$
VIII. $K_2UO_2(SO_4)_2 \cdot 2H_2O$.

RIMBACH[5] has prepared:

IX. $K_4UO_2(SO_4)_3 \cdot 2H_2O$
X. $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$
XI. $Rb_4UO_2(SO_4)_3 \cdot 2H_2O$,

and DE CONINCK[6] has obtained:

XII. $Cs_2UO_2(SO_4)_2 \cdot 2H_2O$.

Of these TRAILL[7] has recently made an X-ray diffraction study of I, IV, and VIII.

We have repeated some of these investigations in an attempt to find suitable crystals for crystal structure analysis. Among the crystals obtained from cesium uranyl sulphate solutions, a new compound was recognized forming quite insoluble crystals of tetragonal symmetry. It proved to be anhydrous, with the formula:

XIII. $Cs_2(UO_2)_2(SO_4)_3$.

So far as is known, no such compound has previously been described. MORTON and BOLTON[8] have said that III, when heated, forms $(NH_4)_2(UO_2)_2(SO_4)_3$, but its relation to XIII is not known. Since XIII has a layer structure, the compounds III and VII may by analogy have similar structures.

Compounds VIII and X were also prepared. X-ray single crystal data and optical data for VIII are identical to that given by TRAILL. X-ray and optical data for X found in the present study, are as follows:

X-ray data	Optical data
Orthorhombic, *Pbnm* (D_{2h}^{16}) or *Pbn*2_1 (C_{2v}^{9})	$2V = 60°$
$a = 11{\cdot}50 \pm 0{\cdot}02$ Å	$\beta = 1{\cdot}572 \pm 0{\cdot}003$
$b = 13{\cdot}48 \pm 0{\cdot}02$ Å	$\alpha = 1{\cdot}568 \pm 0{\cdot}003$
$c = 7{\cdot}42 \pm 0{\cdot}02$ Å	$\gamma = 1{\cdot}605 \pm 0{\cdot}003$
Cell content:	Optical orientation:
$4[Rb_2UO_2(SO_4)_2 \cdot 2H_2O]$	$X = b$, $Y = a$

[3] A. COLANI, *C.R. Acad. Sci., Paris* **185**, 273 (1927).
[4] A. COLANI, *Bull. Soc. Chim.* **43**, 754 (1928).
[5] E. RIMBACH, *Ber. Dtsch. Chem. Ges.* **37**, 461 (1904).
[6] F. W. O. DE CONINCK, *Bull. Belg. Acad.* 94 (1905).
[7] R. J. TRAILL, *Amer. Mineral.* **37**, 394 (1952).
[8] H. MORTON and H. C. BOLTON, *Chem. News* **28**, 50 (1873).

$Rb_2UO_2(SO_4)_2 \cdot 2H_2O$ crystallizes as thin tablets on (010). The calculated and measured specific gravities are 3·87 and 3·82, respectively. X-ray precession photographs of this material show spots which are streaked parallel to b^*, indicating a disordered structure in the b direction.

The present paper is mainly concerned with the determination of the crystal structure of XIII, cesium biuranyl trisulphate.

PREPARATION OF THE CRYSTALS

$Cs_2(UO_2)_2(SO_4)_3$ crystals were synthesized by slow evaporation at room temperature of aqueous solutions containing 1 g of $UO_2SO_4 \cdot 3H_2O$ and 0·8 g of Cs_2SO_4 in 20 ml of water. The material crystallized as minute tetragonal tablets flattened on (001) and bounded by the form (110). The tablets, which usually are about 0·1 mm in size, show perfect (001) cleavage. The crystals are uniaxial negative, $\omega = 1{\cdot}643 \pm 0{\cdot}003$ and $\varepsilon = 1{\cdot}615 \pm 0{\cdot}003$. Their color is light yellow, with no noticeable pleochroism. The specific gravity as determined with the Berman balance is $4{\cdot}74 \pm 0{\cdot}05$ in good agreement with the value of $4{\cdot}80 \pm 0{\cdot}03$ calculated from the unit cell dimensions.

Chemical analysis of the compound (B. L. Ingram, U.S. Geological Survey, analyst) gave the following results: Found: Cs_2O, 25·9; UO_3, 51·9; SO_3, 21·9; H_2O, <0·05; Calc: Cs_2O, 25·76: UO_3, 52·29; SO_3, 22·95; H_2O, 0·0%.

COLLECTION OF X-RAY DATA

The crystallography of $Cs_2(UO_2)_2(SO_4)_3$ was determined from Buerger precession photographs made with MoK_α radiation. Photographs of the ($kh0$), ($kh1$), ($0kl$), ($1kl$), and (hhl) reciprocal lattice nets were made. The patterns show tetragonal symmetry and the only systematic absences observed were ($h00$) reflections where h is odd. The space group therefore must either be $P\bar{4}2_1m$ (D_{2d}^3) or $P42_12$ (D_4^3). The following unit cell data were obtained: $a = 9{\cdot}62 \pm 0{\cdot}02$ Å, $c = 8{\cdot}13 \pm 0{\cdot}01$ Å, $V = 752$ Å^3; $Z = 2$ formulae. Table 1 gives the X-ray powder data for this compound.

Intensity data were obtained for the ($hk0$) and ($0kl$) zones. Lorentz and polarization corrections were determined by the use of a transparent overlay based on the chart prepared by Waser.[9] No absorption corrections were applied to the intensity data, although the effect was minimized by the use of a small crystal (0·1 × 0·1 × 0·05 mm). For the case at hand, the ($hk0$) reciprocal lattice net is parallel to the thin direction of the crystal so that the absorption error for the ($hk0$) intensity data is further reduced, as shown by Donnay and Donnay[10]. Seventy-one nonequivalent ($hk0$) reflexions and 119 nonequivalent ($0kl$) reflexions were measured visually with a calibrated intensity strip prepared with the same camera used to make the photographs.

SOLUTION OF THE STRUCTURE

The space group of $Cs_2(UO_2)_2(SO_4)_3$, as already mentioned, was found to be either $P42_12$ or $P\bar{4}2_1m$. In either of these space groups, the four uranium and four cesium atoms must lie in special positions, either one four-fold set or two twofold sets each. Reference to standard tables[11] shows that for space group $P42_12$ (No. 90) atoms in any of the special positions will not contribute scattering to certain classes of reflexions, namely those (hkl) and ($hk0$) reflexions with $h + k$ odd, and ($0kl$) reflexions with k odd. For this space group certain of these reflexions should be generally weaker than the others, if uranium atoms are in special positions. Careful examination of the ($hk0$) and ($0kl$) reflexions showed no evidence that any group of reflexions is characteristically weaker than any other. The space group $P\bar{4}2_1m$ (No. 113), on the other hand, has a fourfold position (4e, Table 2) that imposes no extra conditions on the reflexions. For this reason the space group $P\bar{4}2_1m$ was thought to be the most probable one for $Cs_2(UO_2)_2(SO_4)_3$. The solution of the structure has verified this assumption.

[9] J. Waser, *Rev. Sci. Instrum.* **22**, 567 (1951).
[10] G. Donnay and J. D. H. Donnay, *Acta Cryst.* **7**, 619 (1954).
[11] *International Tables for X-Ray Crystallography* pp. 180, 203. International Union of Crystallography, Kynoch Press, Birmingham, England (1952).

TABLE 1.—X-RAY POWDER DATA FOR $Cs_2(UO_2)_2(SO_4)_3$*

Measured		Calculated		Measured		Calculated	
I	*d* (Å)	*d* (Å)	*hkl*	*I*	*d* (Å)	*d* (Å)	*hkl*
50	8·11	8·127	001	15	1·897	1·900	323
		6·800	110			1·886	510
13	6·22	6·207	101	18	1·870	1·872	204, 501, 431
71	5·20	5·215	111	18	1·836	1·837	511, 214
5	4·81	4·808	200			1·798	403
18	4·30	4·300	210			1·786	520
100	4·12	4·138	201	13	1·765	1·767	413
		4·063	002			1·756	512
71	3·79	3·801	211			1·744	224, 521
50	3·73	3·743	102	26	1·740	1·738	502, 432, 333
100	3·48	3·488	112	2	1·711	1·716	304
50	3·39	3·401	220			1·700	440
		3·136	221	8	1·685	1·689	314
26	3·09	3·104	202			1·684	423
9	3·03	3·042	310			1·664	441
36	2·973	2·982	301	6	1·647	1·649	530
		2·954	212			1·625	005
9	2·844	2·848	311	9	1·616	1·616	531, 324
8	2·702	2·709	003			1·603	105, 600
		2·667	320	18	1·580	1·581	610, 115
6	2·603	2·607	222, 103			1·572	601
		2·534	321	3	1·566	1·568	104
36	2·511	2·517	302, 113			1·567	433
13	2·433	2·435	312			1·552	611, 404
5	2·401	2·404	400			1·548	513
6	2·359	2·360	203			1·540	205
6	2·329	2·332	410	13	1·531	1·532	414
		2·305	401			1·528	532
18	2·289	2·292	213			1·521	620
		2·266	330			1·520	215
		2·242	411	9	1·512	1·513	334
36	2·229	2·230	322			1·502	540, 612
6	2·183	2·183	331	9	1·491		
1	2·148	2·150	420	2	1·465		
5	2·115	2·119	223	5	1·448		
18	2·073	2·079	421	5	1·431		
		2·069	402, 303	13	1·409		
		2·032	004	18	1·380		
26	2.023	2·023	412, 313	2	1·364		
5	1·979	1·979	332	6	1·340		
		1·963	422	9	1·327		
13	1·943	1·947	114	6	1·291		
		1·923	430				

Not calculated below $d = 1·500$ Å.

* Cu$K\alpha$ radiation, $\lambda = 1·5418$ Å; max. observable *d*, 12 Å. Camera dia. 114·6 mm. Intensities were estimated visually by comparison with a calibrated intensity strip.

To locate the four uranium atoms and possibly the four cesium atoms, Patterson projections were made normal to (001) and (100). These two projections are shown in Figs. 1 and 2, respectively. To interpret the Patterson map on (001), it was assumed, to

Table 2.—Equivalent positions and conditions limiting possible reflexions of space group $P42_1m^{(11)}$ (origin at $\bar{4}$)

Position	Co-ordinates	Conditions
8*f*	x, y, z; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; $\bar{x}, \bar{y}, z$; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\bar{y}, x, \bar{z}$; $\frac{1}{2}+y, \frac{1}{2}+x, z$; $y, \bar{x}, \bar{z}$; $\frac{1}{2}-y, \frac{1}{2}-x, z$.	$h00$: $h = 2n$ (general)
4*e*	$x, \frac{1}{2}+x, z$; $\bar{x}, \frac{1}{2}-x, z$; $\frac{1}{2}+x, \bar{x}, \bar{z}$; $\frac{1}{2}-x, x, \bar{z}$.	no extra conditions
4*d*	$0, 0, z$; $0, 0, \bar{z}$; $\frac{1}{2}, \frac{1}{2}, z$; $\frac{1}{2}, \frac{1}{2}, \bar{z}$.	hkl : $h + k = 2n$
2*c*	$0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$.	$hk0$: $h + k = 2n$
2*b*	$0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.	hkl : $h + k = 2n$
2*a*	$0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$.	hkl : $h + k = 2n$

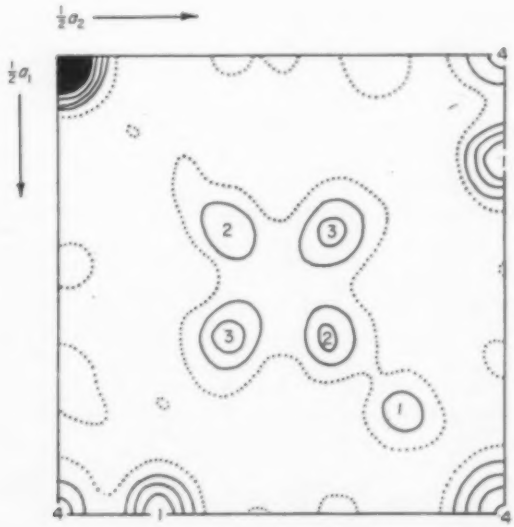

Fig. 1.—Patterson projection on (001) of $Cs_2(UO_2)_2(SO_4)_3$.

start, that the four uranium atoms were in positions 4*e* (Table 2). Uranium–uranium interactions for such positions correspond to peaks No. 1 in Fig. 1. The cesium–cesium and cesium–uranium interactions were identified by assuming that the four cesium

atoms were in twofold positions (positions 2*c* and 2*b*, Table 2). By placing the heavy atoms in these special positions the peaks in Fig. 1 may be identified as follows:

peaks No. 1—Uranium–uranium interactions
peaks No. 2—Cesium(1)–uranium interactions
peaks No. 3—Cesium(2)–uranium interactions
peaks No. 4—Cesium-cesium interactions

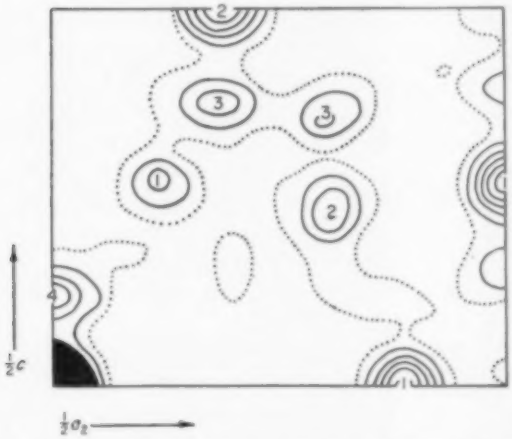

FIG. 2.—Patterson projection on (100) of $Cs_2(UO_2)_2(SO_4)_3$.

These peak assignments are consistent with the following co-ordinates for the heavy atoms:

$$4U \text{ in } 4e \text{ at } x = 0{\cdot}19, \quad y = 0{\cdot}31$$
$$2Cs_1 \text{ in } 2c \text{ at } x = 0, \quad y = \tfrac{1}{2}$$
$$2Cs_2 \text{ in } 2b \text{ at } x = 0, \quad y = 0$$

The expected and experimental relative peak heights in this projection are in reasonable agreement.

The Patterson projection on (100) was readily interpreted by assuming peaks No. 1 (Fig. 2) are uranium–uranium interactions. The remaining peaks on the map were then identified as shown, the peak numbers having the same significance as in Fig. 1. These peak assignments are consistent with the following co-ordinates for the heavy atoms:

$$4U \text{ in } 4e \text{ at } y = 0{\cdot}31, \quad z = 0{\cdot}86$$
$$2Cs_1 \text{ in } 2c \text{ at } y = \tfrac{1}{2}, \quad z = 0{\cdot}37$$
$$2Cs_2 \text{ in } 2b \text{ at } y = 0, \quad z = \tfrac{1}{2}.$$

The expected and experimental relative peak heights are in agreement.

Although the space group $P\bar{4}2_1m$ is non-centrosymmetric, the phases of the (*hk*0) and (0*kl*) structure factors are real if a suitable origin is chosen (at $\bar{4}$ and at $-\frac{1}{4},\frac{1}{4},0$ from $\bar{4}$, respectively). These respective origins were used to simplify the calculation of Fourier syntheses and structure factors, and the listing of the structure factors in Table 4.

Signs were calculated for 61 ($hk0$) reflexions and 88 ($0kl$) reflexions on the basis of the heavy atom positions given above. Fourier projections on (001) and (100) confirmed the positions of the heavy atoms given by the Patterson maps and also resolved the sulphur atoms and a number of oxygen atoms. A model was then made of the structure and tentative positions assigned to all atoms. On the basis of the positions of all the atoms (as obtained from the preliminary Fourier maps and from the model) structure factors were calculated. The temperature and scaling factors were determined together by the method of least squares to obtain the best fit. For the ($hk0$) zone, $B = 1{\cdot}03$ Å^2 and for the ($0kl$) zone, $B = 0{\cdot}85$ Å^2.

The contributions of the uranium and cesium atoms to the structure factors were then calculated and subtracted from the scaled observed structure factors. Subtraction syntheses using the remainders for amplitudes, projected on (001) and (100), yielded the positions of most of the light atoms. Severe overlap (e.g. S_1 and O_4 in the x, y projection; O_1 and O_5 in the y, z projection) prevented the measurement of certain of the light atom parameters from these maps with accuracy. There was also considerable evidence for large variations in the individual temperature motions of the different atoms, and also anistotropic thermal motion, especially of the cesium atoms. At this stage, the reliability factors stood at 0·137 for the ($hk0$) data and 0·143 for the ($0kl$) data (omitting non-observed reflexions).

The data were next subjected to least squares analysis, using a programme written for the Burroughs 205 digital computer. This programme is written to determine individual isotropic temperature parameters for each atom, and is based on the assumption that the nondiagonal terms of the normal equations can be neglected. This calculation, carried through eleven cycles each for the ($hk0$) and ($0kl$) data separately, reduced the reliability factors to 0·053 for the former and 0·096 for the latter. Nevertheless, these results could not be accepted as final, for two reasons. First, the internal consistency in the oxygen parameters, from one projection to the other and within each projection (the calculation was carried out in an orthorhombic space group to facilitate computer programming), indicated an uncertainty in the oxygen positions of as much as 0·2 Å. Second, the sulphur–oxygen distances in the sulphate groups varied from 1·52 to 1·67 Å (using co-ordinates averaged from the least squares results), showing a larger variation and larger average than would be expected for these distances. The main contribution of the least squares calculation seems to have been an evaluation of the individual temperature factors of the atoms, which vary from $B = 0{\cdot}45$ for the sulphur atoms to $B = 3{\cdot}00$ for Cs_2.

The final table of parameters was determined by a judicious analysis of the information supplied by spatial limitations, the least squares calculation, and a new set of subtraction electron-density maps. These maps were prepared taking account of the thermal motions indicated by the least squares analysis, and are shown in Figs. 3 and 4. The final parameters were chosen so that the sulphur–oxygen distances lie between 1·48 and 1·51 Å. With this restriction, the parameters were adjusted to give the best fit to the subtraction maps. These parameters for the most part were consistent with those obtained by least squares analysis, within the observed variations. With the temperature factors averaged from those given by the least squares calculation, the final set of parameters was established, as shown in Table 3A. The errors listed in Table 3B are estimated mainly on the basis of the least squares calculation, and comparisons of internal consistency. The structure factors based on the parameters of

Vol. 15 1960

Table 3A are listed in Table 4, and give a reliability factor of 0·059 for the (*hk*0) reflexions and 0·109 for the (0*kl*) reflexions (omitting non-observed reflexions, and reflexions (220), (001) and (012) because of apparent extinction effects).

DESCRIPTION OF THE STRUCTURE

Cesium biuranyl trisulphate has a layer structure, the layers being composed of

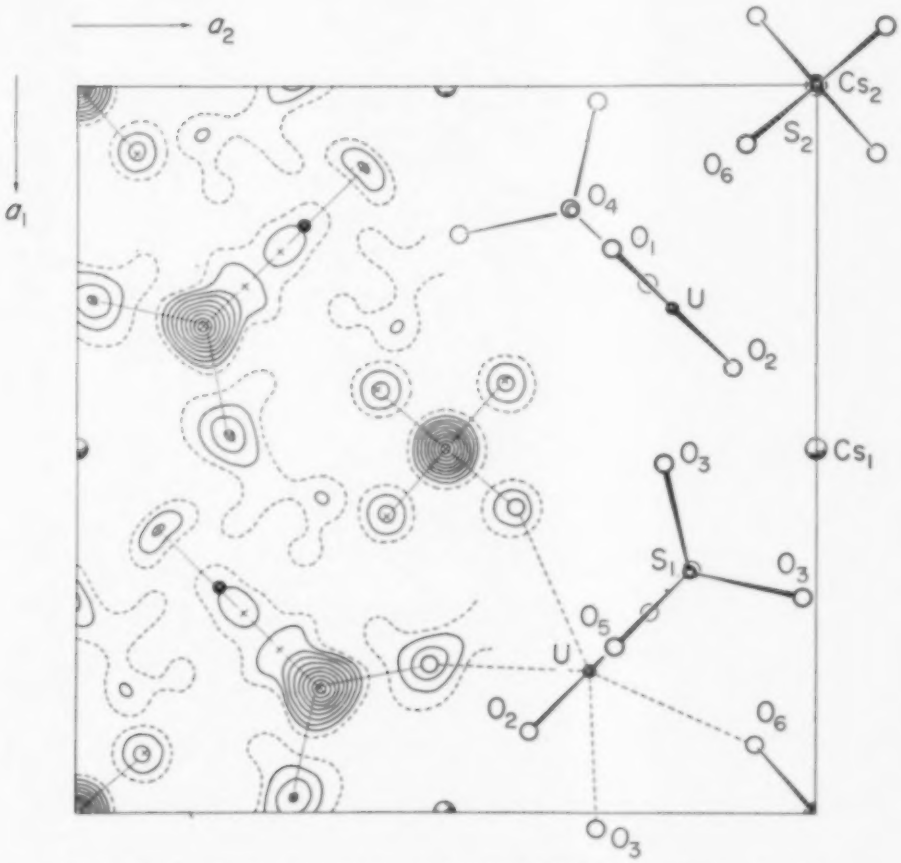

FIG. 3.—Electron-density subtraction map projected on (001) of $Cs_2(UO_2)_2(SO_4)_3$. Contributions of uranium and cesium atoms have been subtracted from the structure amplitudes. Broken contour, 4 electrons/Å^2; contour interval, 4 electrons/Å^2. Atomic positions are identified at the right, and indicated by crosses at the left where electron density is shown.

sulphate and uranyl groups linked together in a complex manner. The layers, consisting of sheets of composition $[(UO_2)_2(SO_4)_3]_n^{2n-}$ parallel to (001), are tied together by cesium ions. Such a structure accounts for the perfect cleavage observed parallel to the tetragonal base. The general features of the structure are illustrated in Fig. 5.

In the $Cs_2(UO_2)_2(SO_4)_3$ structure, there are two crystallographically different types of sulphate groups: the $(SO_4)_M^{2-}$ group lies on the mirror plane (four per unit cell) and the $(SO_4)_C^{2-}$ group lies on the $\bar{4}$ inversion centre (two per cell). The $(SO_4)_M^{2-}$ group

lies with one tetrahedral face nearly parallel with the (001) plane. As described above, the final structure was defined partly on the assumption that the sulphur–oxygen distances in the sulphate groups lie between 1·48 and 1·51 Å. There are surprisingly few accurate structure determinations of sulphate compounds from which we may deduce its probable dimensions. Hanic[12] has reviewed the published structures and concludes that the best value for the sulphur–oxygen distance in the sulphate group is 1·50 Å. Probably the best structure determination for our purposes is that of gypsum

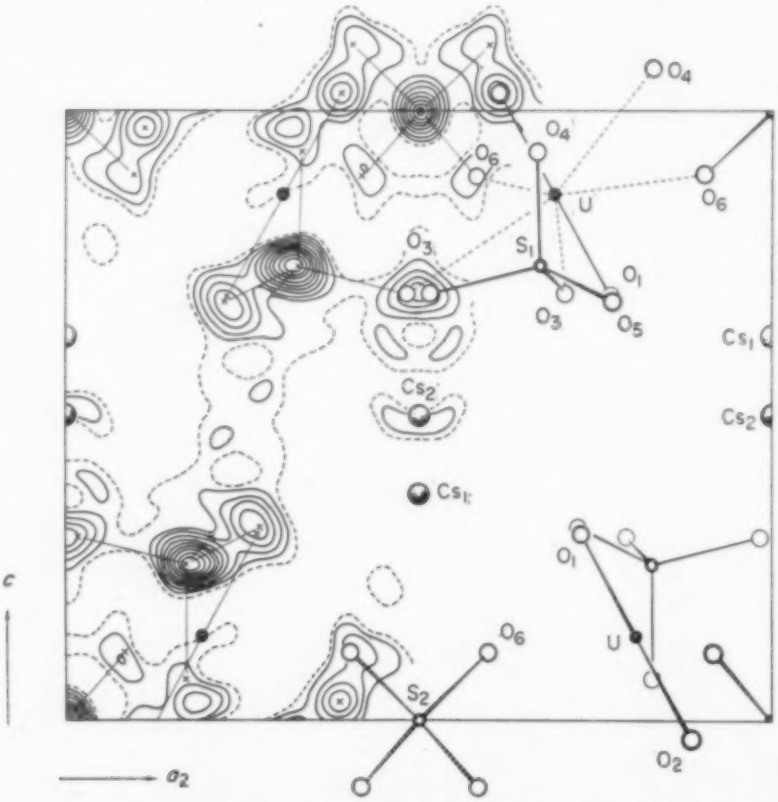

Fig. 4.—Electron-density subtraction map projected on (100) of $Cs_2(UO_2)_2(SO_4)_2$. Data as for Fig. 3.

($CaSO_4 \cdot 2H_2O$) by neutron diffraction, described by Atoji and Rundle[13]. They found distances of 1·49 ± 0·014 and 1·48 ± 0·010 Å for the two crystallographically different sulphur–oxygen distances. It seems reasonable to expect that complex bonding of the sulphate groups to the uranyl groups will not appreciably increase the sulphur–oxygen distance above a value of 1·51 Å.

One of the uranyl oxygen atoms (O_1) is well resolved in both projections, and is found at a distance of 1·74 ± 0·10 Å from the uranium atom. The other is not well resolved in either projection, and has been located so that the uranyl group is

[12] F. Hanic, *Chem. Zvesti* **10**, 268 (1956).
[13] M. Atoji and R. E. Rundle, *J. Chem. Phys.* **29**, 1306 (1958).

Vol. 15 1960

symmetrical and linear. The uranyl group lies in the mirror plane and is tilted 38° from the z direction. Oxygen atoms from five different sulphate groups are bonded to the uranyl group to form a pentagon lying in a plane nearly perpendicular to the axis of the uranyl group. The co-ordination polyhedron around the uranium atom is thus a nearly regular pentagonal bipyramid. The dimensions of this configuration are as follows:

Bond	Length	Angle to U–O_1
U–O_3 (2)	2·47 ± 0·10 Å	86° ±5°
U–O_4	2·46	93°
U–O_6 (2)	2·37	81°

TABLE 3.—PARAMETERS FOR $Cs_2(UO_2)_2(SO_4)_3$ ORIGIN AT $\bar{4}$ IN SPACE GROUP $P\bar{4}2_1m$

A. PARAMETERS (REDUNDANT PARAMETERS IN PARENTHESES)

Atom	x	y	z	B(Å²) ($hk0$)	B(Å²) ($0kl$)	Group
4U in e	0·1930	(0·3070)	0·8646	0·67	0·78	UO_2^{+2}
2Cs_1 in c	0	½	0·3685	1·90	1·65	Cs_1^+
2Cs_2 in b	0	0	½	3·00	2·50	Cs_2^+
4S_1 in e	0·330	(0·170)	0·252	0·60	0·45	$(SO_4)_M^{-2}$
2S_2 in a	0	0	0	0·60	0·45	$(SO_4)_O^{-2}$
4O_1 in e	0·273	(0·227)	0·698	1·50		UO_2^{+2}
4O_2 in e	0·113	(0·387)	0·031	1·50		UO_2^{+2}
8O_3 in f	0·295	0·022	0·300	2·50		$(SO_4)_M^{-2}$
4O_4 in e	0·327	(0·173)	0·068	3·00		$(SO_4)_M^{-2}$
4O_5 in e	0·225	(0·275)	0·315	2·10		$(SO_4)_M^{-2}$
8O_6 in f	0·096	0·082	0·890	1·00		$(SO_4)_O^{-2}$

B. ESTIMATED STANDARD DEVIATIONS OF PARAMETERS

Atom	x, y	z	x, y, z, (Å)	B(Å²)
U	0·0003	0·0003	0·003	0·05
Cs	0·0012	0·0015	0·012	0·20
S	0·0026	0·0030	0·025	0·40
O	0·010	0·012	0·10	1·5

The oxygen–uranium–oxygen angles within the pentagon are 71° (4) and 78° (O_3–U–O_3'). The pentagonal bipyramid is now well established as a characteristic co-ordination configuration for U(VI). The $Cs_2(UO_2)_2(SO_4)_3$ structure represents the fifth example of fivefold co-ordination determined for the uranyl group. Other structures showing this configuration are $K_3UO_2F_5$,[14] $Ca(H_2O)_2(UO_2)_2(SiO_4)_2{\cdot}3H_2O$ (uranophane),[15] $Cu(UO_2)_2(SO_4)_2(OH)_2{\cdot}6H_2O$ (johannite),[16] and $K_2(UO_2)_2V_2O_8$ (analogue of carnotite).[17]

[14] W. H. ZACHARIASEN, *Acta Cryst.* **7**, 783 (1954).
[15] D. K. SMITH, JR., J. W. GRUNER and W. N. LIPSCOMB, *Amer. Mineral.* **42**, 594 (1957).
[16] D. E. APPLEMAN, *Bull. Geol. Soc. Amer.* **68**, 1696 (1957).
[17] D. E. APPLEMAN and H. T. EVANS, JR., *Acta Cryst.* **10**, 765 (1957).

The distribution of bonds in the pentagonal bipyramid cannot be estimated with much certainty, because of the rather large errors associated with the uranium–oxygen distances obtained in this structure determination. Nevertheless, it can be shown that they are approximately reasonable in terms of the relation between bond number and bond length as plotted by Zachariasen[18]. An empirical logarithmic function such

Table 4.—Structure factors for $Cs_2(UO_2)_2(SO_4)_3$

A. ($hk0$) reflexions : origin at $\bar{4}$

($hk0$)	F(obs.)	F(calc.)*	($hk0$)	F(obs.)	F(calc.)*
2 0 0	88	−80	9 3 0	19	−29
4 0 0	220	206	10 3 0	43	−39
6 0 0	269	266	11 3 0	106	97
8 0 0	97	−95	12 3 0	44	45
10 0 0	223	221			
12 0 0	18	20	4 4 0	215	209
			5 4 0	29	25
1 1 0	30	−24	6 4 0	124	125
2 1 0	150	−143	7 4 0	112	−114
3 1 0	175	162	8 4 0	71	72
4 1 0	196	212	9 4 0	175	154
5 1 0	129	−124	10 4 0	78	78
6 1 0	153	−180	11 4 0	103	−106
7 1 0	35	38	12 4 0	21	24
8 1 0	74	79			
9 1 0		16	5 5 0	218	−218
10 1 0	37	38	6 5 0	31	36
11 1 0	33	−31	7 5 0	118	122
12 1 0	101	−106	8 5 0	38	28
13 1 0	36	45	9 5 0	16	21
			10 5 0		9
2 2 0	346	414	11 5 0	96	99
3 2 0	64	−64			
4 2 0	102	105	6 6 0	198	202
5 2 0		−8	7 6 0	116	110
6 2 0	24	13	8 6 0	29	−29
7 2 0	72	67	9 6 0	108	−117
8 2 0	236	229	10 6 0	103	106
9 2 0	112	−106	11 6 0	66	66
10 2 0	27	−20			
11 2 0	76	74	7 7 0	51	−53
12 2 0	82	78	8 7 0	45	48
			9 7 0		5
3 3 0	217	−237	10 7 0	23	32
4 3 0	134	−127	11 7 0	28	33
5 3 0	240	238			
6 3 0	96	99	8 8 0	167	194
7 3 0	80	−78	9 8 0	46	44
8 3 0	24	−25	10 8 0	48	55
			9 9 0	22	30

[18] W. H. Zachariasen, *Acta Cryst.* **12**, 526 (1959).

Vol. 15 1960

Table 4 (continued)

B. (0*kl*) REFLEXIONS : ORIGIN AT $\frac{1}{4}$, $\frac{1}{4}$, 0 FROM $\bar{4}$

(0*kl*)	*F*(obs.)	*F*(calc.)*	(0*kl*)	*F*(obs.)	*F*(calc.)*	(0*kl*)	*F*(obs.)	*F*(calc.)*
0 2 0	86	79	0 8 3	161	154	0 0 7	106	119
0 4 0	232	208	0 9 3		−7	0 1 7	12	−13
0 6 0	279	−270	0 10 3	93	91	0 2 7	210	193
0 8 0	99	−86	0 11 3	20	−17	0 3 7	100	−109
0 10 0	208	−223	0 12 3	43	42	0 4 7	39	−27
						0 5 7	43	−40
			0 0 4	169	−205	0 6 7	23	−22
0 0 1	89	134	0 1 4	17	−20	0 7 7	37	−38
0 1 1	69	65	0 2 4	141	−162	0 8 7	160	−150
0 2 1	239	265	0 3 4	39	−45	0 9 7		23
0 3 1	288	290	0 4 4	26	−18	0 10 7	81	−69
0 4 1	163	−150	0 5 4	46	−44			
0 5 1	189	159	0 6 4	43	49	0 0 8	257	233
0 6 1		18	0 7 4	30	−31	0 1 8	49	38
0 7 1	107	103	0 8 4	145	146	0 2 8	24	16
0 8 1	182	−180	0 9 4		−16	0 3 8	52	48
0 9 1	65	−74	0 10 4	115	124	0 4 8	81	64
0 10 1	66	−56	0 11 4	14	16	0 5 8	105	84
0 11 1	68	−73	0 12 4	44	53	0 6 8	139	−140
0 12 1	39	−53				0 7 8	25	28
0 13 1	77	−102	0 0 5	175	−190	0 8 8	66	−60
			0 1 5		−4			
0 0 2		−6	0 2 5	65	−86	0 0 9		6
0 1 2	142	187	0 3 5	164	−181	0 1 9		20
0 2 2	162	−187	0 4 5	35	−34	0 2 9	53	44
0 3 2	185	188	0 5 5	84	−91	0 3 9	182	164
0 4 2	45	34	0 6 5	32	30	0 4 9	26	−26
0 5 2	318	307	0 7 5	119	−126	0 5 9	122	108
0 6 2		−22	0 8 5	64	74	0 6 9		20
0 7 2	75	67	0 9 5		9	0 7 9	116	85
0 8 2	86	89	0 10 5	45	54			
0 9 2	25	34	0 11 5	42	40	0 0 10	67	−55
0 10 2	28	−30				0 1 10	52	55
0 11 2	113	−120	0 0 6	131	125	0 2 10	108	−82
0 12 2		17	0 1 6	144	−134	0 3 10	49	53
0 13 2	59	−81	0 2 6	22	−25	0 4 10		21
			0 3 6	91	−103	0 5 10	141	108
0 0 3	121	−150	0 4 6	98	103			
0 1 3	38	−32	0 5 6	183	−193	0 0 11	114	−96
0 2 3	109	−132	0 6 6	55	−63	0 1 11	17	−14
0 3 3	144	161	0 7 6	39	−35			
0 4 3		12	0 8 6	13	17			
0 5 3	71	72	0 9 6		−23			
0 6 3	79	79	0 10 6	71	−78			
0 7 3	112	106	0 11 6	84	99			

*F (calc.) based on parameters of Table 3.

as that used by Pauling[19] for intermetallic compounds, may be fitted to Zachariasen's curve. The formula is

$$D_1 - D_n = 2k \log n$$

where n is the bond number, D_n is the interatomic distance, D_1 is the distance for unit bond number and k is a constant. A good fit to the curve (based on various published structures of uranyl complexes) is obtained with $D_1 = 2{\cdot}03$ Å and $k = 0{\cdot}45$ (for

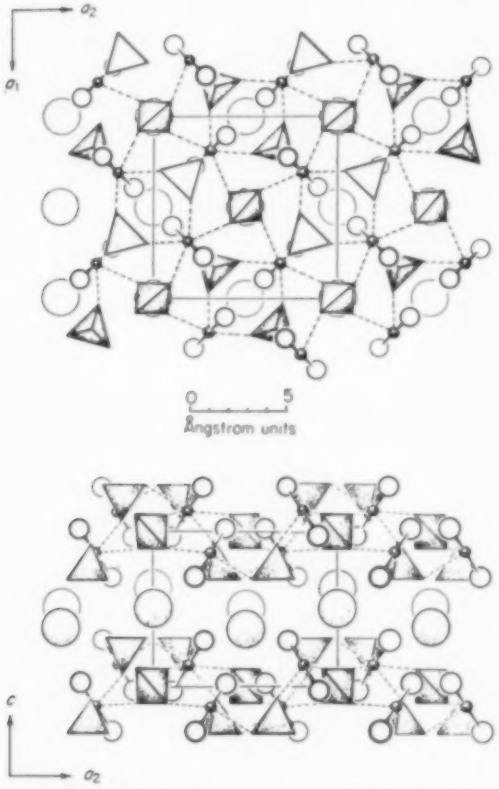

Fig. 5.—Schematic views along [001] and [100] of the crystal structure of $Cs_2(UO_2)_2(SO_4)_3$. Uranyl groups are indicated by dumbbell-shaped figures, cesium atoms by large open circles and sulphate groups as tetrahedra. Co-ordination of sulphate groups to uranyl groups is indicated by broken lines.

metals Pauling used $k = 0{\cdot}300$). Using this function, the distribution of bond numbers in the pentagonal bipyramid of $Cs_2(UO_2)_2(SO_4)_3$ is as follows:

Bond	Length	Number
$U–O_3$	2·47	0·32 (×2)
$U–O_4$	2·46	0·33
$U–O_6$	2·37	0·42 (×2)
$U–O_1$	1·74	2·10
$U–O_2$	1·74	2·10
	Total	6·01

[19] L. Pauling, *J. Amer. Chem. Soc.* **69**, 542 (1947).

Vol. 15 1960

Thus, a satisfactory check with the uranium valency is obtained, consistent with bond distributions found by ZACHARIASEN for other uranyl complex structures. A nearly pure double bond is indicated for each of the two uranyl–oxygen bonds of the uranyl group.

The Cs_2 atom is in twelvefold co-ordination with oxygen atoms as follows:

Cs_2–O_1	3·42 ± 0·10 Å
Cs_2–O_3	3·28
Cs_2–O_6	3·40

There are four of each of these contacts around each Cs_2 atom, and, in addition to the twelve near neighbours, there are four more (O_5) at 3·74 Å. This atom is thus enclosed in a large cage of oxygen atoms and is therefore rather loosely bound. The high temperature factor found for Cs_2 ($B = 2{\cdot}75$ Å^2, ave.) as compared with Cs_1 ($B = 1{\cdot}75$, ave.) is undoubtedly a result of this loose co-ordination. The Cs_1 atom is more tightly bound, in eightfold co-ordination, as follows:

Cs_1–O_1	(2)	3·14 ± 0·10 Å
Cs_1–O_2	(2)	3·15
Cs_1–O_3	(4)	3·35

The next nearest neighbour is O_4 at 4·26 Å. Unfortunately, no accurate structure determinations of other cesium compounds have been published with which to compare these distances. The sum of the ionic radii of Cs^+ and O^{2-} as given by PAULING is 3·09 Å.

Acknowledgements—The authors are especially indebted to D. E. APPLEMAN for making the necessary computations for the solution of this structure. Grateful acknowledgement is also made to B. L. INGRAM for the chemical analysis, to D. R. ROSS for the X-ray powder analysis, and to C. S. ROSS for the determination of the optical properties. We wish especially to acknowledge the assistance and interest of Professor G. M. BROWN of the Department of Chemistry, University of Maryland. The work is part of a programme being conducted by the U.S. Geological Survey on behalf of the Division of Research of the U.S. Atomic Energy Commission.

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 352 to 355. Pergamon Press Ltd.

PREPARATION AND CRYSTALLOGRAPHIC STUDY OF SOME NEW RARE EARTH COMPOUNDS

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Abstract—With the exception of element 61 the tervalent rare earth ions, as well as those of scandium and yttrium, have been incorporated in the formula type $BaNb_{0\cdot5}Me_{0\cdot5}O_3$ (Me = rare earth metal Sc and Y). All compounds crystallize in the undistorted perovskite structure, except for $BaLa_{0\cdot5}Nb_{0\cdot5}O_3$, which is tetragonally distorted at room temperature but cubic at 800°C. Lattice parameters, densities and dielectric properties have been determined and are summarized.

THE size of the tervalent rare earth ions as computed on the basis of empirical assumptions by GOLDSCHMIDT[1] (1·15 Å for La^{3+} to 0·99 Å for Lu^{3+}) is such that in the perovskite structure it can occupy both the A and B-sites. GELLER,[2] for instance, reported rare earth ferrates, chromates and aluminates of the type ABO_3, where A = rare earth, B = Fe, Cr, Al. These compounds crystallize in orthorhombic or rhombohedral forms, in very close structural relationship to the undistorted cubic perovskite. If larger and more basic ions than the rare earth ions, such as Ba^{2+} or Sr^{2+}, are introduced in the ABO_3 structure together with the rare earths, the latter are forced into the octahedrally coordinated B-sites. However, only 50 mole per cent of a rare earth ion can be incorporated, since 50 mole per cent of a five-valent ion of proper size have to occupy half of the B-sites in order to render the total valence of positive ions six, thus restoring electroneutrality. Compounds such as $A^{2+}(B_1^{5+})_{0\cdot5}(B_2^{3+})_{0\cdot5}O_3$, where B_2 can be a rare earth ion, have recently been theoretically postulated by SMOLENSKI[3]. As possible rare earth ions SMOLENSKI enumerated Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}. He did not list the ions from La^{3+} to Gd^{3+}, probably because on the basis of GOLDSCHMIDT's equation, governing the perovskite structure [$t = (r_A + r_O)/2(r_B + r_O) = 0{\cdot}8 \leqslant t \leqslant 1{\cdot}05$] the tolerance factor exceeded the given limit. Since, with the exception of $BaLa_{0\cdot5}Nb_{0\cdot5}O_3$, which is tetragonally distorted at room temperature, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Gd^{3+} also do form true perovskites, one can see that the limitations of t should not be considered as binding as the equation might indicate. The question as to a possible ordering in the B-sites has recently been investigated by WOLD[4] for compounds of the type $LaFe_xCr_{1-x}O_3$. On the basis of magnetic measurements they concluded that the B-ions occupy their sites in a random fashion. It appears that for the investigated compounds the same holds true, since the absence of any superstructure lines also indicates a random distribution of the B_1 and B_2 ions.

Since only the rare earth ions were changed in the series of prepared compounds, a relationship between a_0 and the ionic radius of the rare earth ion can be established,

[1] V. M. GOLDSCHMIDT, *Skrifter Norske Videnskaps-Akad. Mat. Naturvid.* **KL. No. 2 (1926).**
[2] S. GELLER and E. A. WOOD, *Acta Cryst.* **9**, 563 (1956).
[3] G. A. SMOLENSKI and A. I. AGRANOVSKAIA, *Izv. Akad. Nauk SSSR* **28, No. 7, 1491 (1958).**
[4] A. WOLD and W. CROFT, *J. Phys. Chem.* **63**, 447 (1959).

Vol. 15 1960

although no absolute values for the B_2^{3+} ions can be computed. From the parameters it becomes obvious that the change in size is not constant from element to element.

EXPERIMENTAL

The rare-earth oxides and yttrium oxide were obtained in 99 per cent+ purity from Research Chemicals Inc. Scandium oxide was prepared from resublimed $ScCl_3$, which in turn was obtained by chlorination of thortveitite from Norsk Feldspat, Norway. High purity Nb_2O_5 (99%+) was purchased from Fansteel and $BaCO_3$ was of Baker's "analysed reagent" grade quality. Cerium, praseodymium and terbium-oxide were obtained in an oxidation state higher than three, and the corresponding sesquioxides were prepared by hydrogen reduction at 1200°C. In order to eliminate the possibility of oxidation during the subsequent reaction of these oxides with Nb_2O_5 and BaO, the preparations were made either under argon, gettered with a Zr–Ti alloy, or *in vacuo*. All other compounds were prepared in air. The components were weighed to the nearest 0·1 mg according to stoicheiometry and mixing was effected by ballmilling in a mechanical agate ball mill under acetone. The dried and filtered mixture was then fired at 1000–1200°C until the theoretical CO_2 loss was observed. The reaction product was then dry ball milled and pressed into a 1 in. diameter pellet under 20,000 lb/in². Whenever BaO was interreacted with the oxides, the mixture was only dry ball milled and directly pressed into a 1 in. diameter pellet. Final firing was carried out for 4–6 hr between 1200° and 1400°C in air, except that for the compounds containing Ce, Pr or Tb it was effected under argon or *in vacuo*.

Analysis

All compounds were analysed for barium and niobium.

Found: Ba, 54·10; Nb, 18·47. Calc. for $BaSc_{0.5}Nb_{0.5}O_3$: Ba, 54·00; Nb, 18·26%.
Found: Ba, 50·03; Nb, 16·87. Calc. for $BaY_{0.5}Nb_{0.5}O_3$: Ba, 49·72; Nb, 16·81%.
Found: Ba, 44·86; Nb, 15·93 Calc. for $BaLa_{0.5}Nb_{0.5}O_3$: Ba, 45·59; Nb, 15·42%.
Found: Ba, 45·62; Nb, 14·98. Calc. for $BaCe_{0.5}Nb_{0.5}O_3$: Ba, 45·50; Nb, 14·98%.
Found: Ba, 45·43; Nb, 15·94. Calc. for $BaPr_{0.5}Nb_{0.5}O_3$: Ba, 45·44; Nb, 15·37%.
Found: Ba, 45·20; Nb, 15·43. Calc. for $BaNd_{0.5}Nb_{0.5}O_3$: Ba, 45·19; Nb, 15·285%.
Found: Ba, 44·82; Nb, 15·90. Calc. for $BaSm_{0.5}Nb_{0.5}O_3$: Ba, 44·74; Nb, 15·31%.
Found: Ba, 45·39; Nb, 15·13. Calc. for $BaEu_{0.5}Nb_{0.5}O_3$: Ba, 44·62; Nb, 15·09%.
Found: Ba, 43·87; Nb, 15·09. Calc. for $BaGd_{0.5}Nb_{0.5}O_3$: Ba, 44·27; Nb, 14·97%.
Found: Ba, 44·32; Nb, 14·98. Calc. for $BaTb_{0.5}Nb_{0.5}O_3$: Ba, 44·18; Nb, 14·94%.
Found: Ba, 43·91; Nb, 14·73. Calc. for $BaDy_{0.5}Nb_{0.5}O_3$: Ba, 43·88; Nb, 14·84%.
Found: Ba, 44·21; Nb, 14·78. Calc. for $BaHo_{0.5}Nb_{0.5}O_3$: Ba, 43·80; Nb, 14·815%.
Found: Ba, 43·48; Nb, 14·34. Calc. for $BaEr_{0.5}Nb_{0.5}O_3$: Ba, 43·55; Nb, 14·225%.
Found: Ba, 43·23; Nb, 14·38. Calc. for $BaTm_{0.5}Nb_{0.5}O_3$: Ba, 43·40; Nb, 14·675%.
Found: Ba, 43·07; Nb, 14·72. Calc. for $BaYb_{0.5}Nb_{0.5}O_3$: Ba, 43·21; Nb, 14·615%.
Found: Ba, 42·99; Nb, 14·61. Calc. for $BaLu_{0.5}Nb_{0.5}O_3$: Ba, 43·02; Nb, 14·55%.

X-ray study

The parameters of the cubic compounds were determined on the basis of powder diffraction patterns obtained with a 114·6 mm Philips camera. All samples were ground to −325 mesh, sealed in 3 mm Lindemann glass capillaries and then exposed to copper K_α radiation ($\lambda = 1{\cdot}5148$ Å) at 25·0°C for 2–4 hr. The readings were taken visually at constant temperature with a Hilger and Watts film measuring rule with 0·05 mm vernier divisions. All films were corrected for film shrinkage, and a_0 was obtained by extrapolating the parameters against $\frac{1}{2}(\cos\theta + \cos^2\theta)/\sin\theta$ according to NELSON and RILEY[8]. The parameters may be considered accurate to ±0·001 Å. The parameter of the tetragonal $BaNb_{0.5}La_{0.5}O_3$ was calculated from a pattern obtained with a Norelco Diffractometer at 26·0°C. The high temperature parameter was obtained from a pattern taken in a Norelco high temperature camera. The parameters are summarized with the electrical data and the densities in Table 1.

[8] T. B. NELSON and D. P. RILEY, *Proc. Phys. Soc.* **57**, 160 (1945).

Density determinations and electrical measurements

The densities were determined on powdered specimen of −200 mesh. The samples were weighed into a 5 ml pycnometer and CCl_4 was distilled onto the sample under vacuum. The electrical measurements were conducted with 1 in. diameter pellets, 1–2 mm thick. The surfaces were coated with No. 4922 du Pont silver paint. Dielectric constants were determined at a frequency of 1 kc/s. Due to errors in measurement of radius and thickness of the sample, and due to non-uniformity of the sample surface, the dielectric constant may be in error to the extent of about 20 per cent.

TABLE 1.—PARAMETERS, DENSITIES, DIELECTRIC CONSTANTS AND RESISTIVITIES OF THE INVESTIGATED COMPOUNDS

No.	Composition	a_0 (Å)	X-ray density (g ml^{-1})	Pycnometer density (g ml^{-1})	Dielectric const.	Resistivity (Ω-cm)
1	$BaSc_{0.5}Nb_{0.5}O_3$	4·121	6·033	5·87	16	$>1·2 \times 10^7$
2	$BaY_{0.5}Nb_{0.5}O_3$	4·180	6·280	6·14	18	$>1·7 \times 10^7$
3	$BaLa_{0.5}Nb_{0.5}O_3$	4·298 ($c_0 = 4·337$)	6·243	6·07	74	$>2·3 \times 10^8$
4	$BaCe_{0.5}Nb_{0.5}O_3$	4·293	6·334	6·31	37	$>2·4 \times 10^8$
5	$BaPr_{0.5}Nb_{0.5}O_3$	4·285	6·379	6·30	67	$>6·0 \times 10^7$
6	$BaNd_{0.5}Nb_{0.5}O_3$	4·277	6·450	6·40	13	$>7·7 \times 10^8$
7	$BaSm_{0.5}Nb_{0.5}O_3$	4·248	6·649	6·52	16	$>1·1 \times 10^9$
8	$BaEu_{0.5}Nb_{0.5}O_3$	4·243	6·690	6·68	20	$>4·0 \times 10^8$
9	$BaGd_{0.5}Nb_{0.5}O_3$	4·242	6·748	6·70	19	$>9·1 \times 10^8$
10	$BaTb_{0.5}Nb_{0.5}O_3$	4·229	6·825	6·79	14	$>2·0 \times 10^8$
11	$BaDy_{0.5}Nb_{0.5}O_3$	4·224	6·897	6·77	13	$>1·0 \times 10^9$
12	$BaHo_{0.5}Nb_{0.5}O_3$	4·216	6·945	6·88	7	$>6·0 \times 10^8$
13	$BaEr_{0.5}Nb_{0.5}O_3$	4·208	7·029	6·92	10	$>1·1 \times 10^9$
14	$BaTm_{0.5}Nb_{0.5}O_3$	4·201	7·088	7·08	10	$>8·3 \times 10^8$
15	$BaYb_{0.5}Nb_{0.5}O_3$	4·192	7·197	7·03	13	$>2·0 \times 10^9$
16	$BaLu_{0.5}Nb_{0.5}O_3$	4·187	7·222	7·01	11	$>4·0 \times 10^8$

Resistivities were determined with an impedance bridge, using a General Type 650-pl oscillator-amplifier as a source of direct current. The maximum resistance limit of the bridge was 1 MΩ; hence for these materials of very high resistivities only a lower limit could be specified. The resistivities may be inaccurate to the extent of 20 per cent; again due to sample irregularities. It has to be remembered also that the resistivities measured apply to sintered compacts with a density of about 80 per cent of theoretical.

DISCUSSION

If one plots the determined parameters against the atomic numbers of the rare earth contained in the various compounds, as done in Fig. 1, the lanthanide contraction is reflected in the graph. The shape of the curve is similar to the curve obtained when the reported ionic radii are plotted against the atomic numbers. There is, however, a smaller spread in change of size for the compounds, since the rare earth ions constitute only a minor fraction of the overall structure. Since the rare earth and niobium ions are apparently randomly distributed over the octahedrally co-ordinated B-sites, only average ionic radii might be calculated. This isostructural series of new rare earth compounds also indicates that there is not a consistent change of ionic radius going from one element to another. The most significant group is that of the elements Sm, Eu and Gd, which obviously exhibit only minor changes in the size of their ionic radii. It is interesting to notice that two out of these three ions may occur in the divalent state and the partial presence of such ions would result in an abnormal lattice parameter.

Vol. 15 1960

At the same time this would cause a slightly oxygen deficient structure, which might help to explain the density discrepancy particularly apparent in the case of the Sm-compound. However, only a detailed magnetic susceptibility study would help to unequivocally clarify the situation.

The room temperature c/a ratio for $BaLa_{0\cdot5}Nb_{0\cdot5}O_3$ of 1·009 is similar to the one of the ferroelectric $BaTiO_3$. Since the dielectric constant of $BaLa_{0\cdot5}Nb_{0\cdot5}O_3$ was also somewhat out of line with the rest of the preparations, the compound was checked for

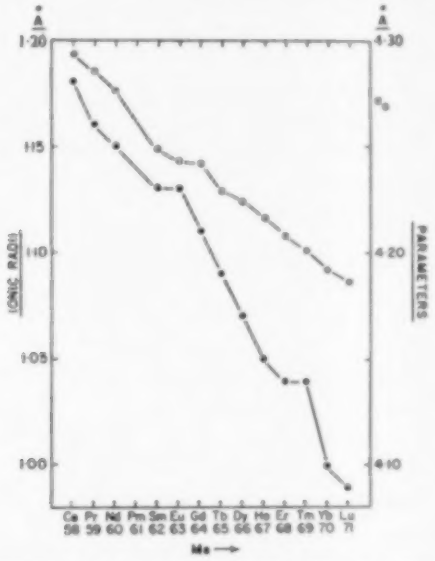

FIG. 1.—Lattice parameters of the compounds $BaMe_{0\cdot5}Nb_{0\cdot5}O_3$ (○) as compared to the published ionic radii of the rare earths (●).

possible ferroelectric behaviour. For this purpose the sample was placed in a ferroelectric loop tracer, described by DIAMANT *et al.*[6] which displays on an oscilloscope a trace of the spontaneous charge-electric field relationship in the sample. If the sample is ferroelectric, a ferroelectric hysteresis loop is observed. The input voltage maximum is near 1800 V and with samples which are 3 mm thick, fields of the order of 600 V/cm can be obtained. $BaLa_{0\cdot5}Nb_{0\cdot5}O_3$ was investigated both at 25°C and at −196°C, and no evidence of ferroelectricity was observed.

If the high dielectric constant is caused by a slight dipole between the octahedrally coordinated ions and the oxygen, the distortion for $BaCe_{0\cdot5}Nb_{0\cdot5}O_3$ and $BaPr_{0\cdot5}Nb_{0\cdot5}O_3$ may be too small to be picked up by conventional X-ray techniques. For these samples, too, no evidence of ferroelectricity was observed.

Acknowledgements—Thanks are due to Dr. R. B. HAND for measuring the resistivities and dielectric constants, to Dr. P. E. BIERSTEDT for checking the compounds for ferroelectricity and to Mr. A. F. MATERA for his assistance in the X-ray work.

[6] H. DIAMANT, K. DRENK and R. PEPINSKY, *Rev. Sci. Instrum.* **28**, 30 (1957).

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 356 to 358. Pergamon Press Ltd.

X-RAY STUDY AND ELECTRICAL PROPERTIES OF THE SYSTEMS $SrMo_xZr_{(1-x)}O_3$ AND $SrMo_xTi_{(1-x)}O_3$

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Abstract—An unlimited number of solid solutions are formed when either the insulator $SrZrO_3$ or $SrTiO_3$ is reacted with the conducter $SrMoO_3$. The solid solutions investigated cover an electrical resistivity range from 10^{-4} ohm cm to 10^8 ohm cm. Seebeck coefficient and resistivity data on several compositions of these systems are reported. $BaMoO_3$ and $BaZrO_3$ apparently do not form solid solutions.

IN a previous publication[1] it was reported that an unlimited number of solid solutions were formed between the two molybdates $SrMoO_3$ and $BaMoO_3$. In that case, of course, substitutions occurred only in the 12-co-ordinated sites, with the 6-co-ordinated Mo^{4+} remaining unchanged. It was of interest to see if a similar substitution would occur at the octahedrally co-ordinated site. However, when attempts were made to prepare solid solutions between $SrMoO_3$ and $SrSnO_3$ (both of perovskite structure), inhomogeneous, gray reaction products resulted which contained quantities of metallic tin. In other words, the redox-potential of the reaction $Mo^{4+} + Sn^{4+}$ at 1200°C is such that Mo^{4+} reduces tetravalent tin to the metallic state. This indicated that, when chemically different species were to be reacted with each other, not only structural but also thermodynamic properties had to be considered. Therefore, the more stable zirconates and titanates, $SrZrO_3$ and $SrTiO_3$, were reacted with $SrMoO_3$. In these cases no chemical reaction took place and solid solutions were formed. The electrical properties of these systems were of particular interest, since they covered the whole resistivity range between conducting and insulating compositions of perovskite structure.

EXPERIMENTAL

(a) *Preparative*

The molybdates $SrMoO_3$ and $BaMoO_3$ were prepared by the method described previously.[1] $SrZrO_3$ and $SrTiO_3$ were prepared by a solid state reaction between $SrCO_3$ and the corresponding metal oxide at 1200°C. After firing at this temperature for 4–6 hr, the reaction product was ball-milled under acetone, pressed into a 1 in. diameter pellet and refired at 1300°C for 6–8 hr.

The preparation of the solid solutions had to be carried out under inert atmosphere (Ti/Zr gettered argon) in order to prevent the molybdates (IV) from oxidizing. The components, in powder form (−200 mesh), were ball-milled together in a mechanical agate mortar and pressed at 20–40 ton/in² into bars ¼ in. square and 2 in. long. These bars were fired at 1200–1400°C for 10–12 hr, which was sufficiently long to insure complete reaction as evidenced by the X-ray diffraction patterns.

(b) *Analyses*

The possibility of oxygen loss or pick-up during the formation of the solid solutions was checked by careful weight control of the reaction boat with the mixture before and after firing. The changes in each case were no larger than 0·4 mg. Specifically, the prefired boat plus reaction mixture for

[1] L. H. BRIXNER, *J. Inorg. Nucl. Chem.* **15**, 352 (1960).

$SrMo_{0\cdot5}Zr_{0\cdot5}O_3$(4·0000 g $SrMoO_3$ + 3·9184 g $SrZrO_3$) weighed 31·0420 g before and 31·0417 g after firing, indicating that there is essentially no weight change, and oxygen is neither picked up nor lost during the interaction. Furthermore, the compositions were analysed for at least one of the metallic constituents: Sr, Mo, Ti, or Zr. Within analytical errors, the composition of the solid solutions corresponded to their theoretical formula. As a typical example, the analysis of $SrMo_{0\cdot75}Zr_{0\cdot25}O_3$ is given: (Found: Sr, 38·10; Mo, 31·17. Calc. for $SrMo_{0\cdot75}Zr_{0\cdot25}O_3$: Sr, 38·03; Mo, 31·24%).

(c) *X-ray study*

Samples of the compositions $SrMo_xZr_{(1-x)}O_3$ and $SrMo_xTi_{(1-x)}O_3$ with x = 1, 0·75, 0·50, 0·25 and 0 were prepared in the manner described above and a specimen for X-ray study was cut from the centre of each of the bars. Powder X-ray diffraction patterns were taken with a Philips 114·6 mm diameter camera at 24·5°C. The samples were sealed in 0·2 mm diameter Lindemann glass capillaries and exposed to copper K_α radiation (λ = 1·5418 Å) for between 4–6 hr. All readings were taken at constant temperature and corrected for film shrinkage. Accurate parameters were obtained by extrapolating a_0 vs $\frac{1}{2}$ ($\cos^2\theta/\sin\theta + \cos^2\theta/\theta$) according to NELSON and RILEY[2]. Tables 1 and 2 summarize the lattice parameters and show that a Vegard's law dependence is observed for both systems.

TABLE 1.—LATTICE PARAMETERS FOR THE SYSTEM $SrMo_xZr_{(1-x)}O_3$

x	a_0 (Å)
1·00	3·9751 ± 0·0003
0·75	4·005 ± 0·001
0·50	4·039 ± 0·001
0·25	4·072 ± 0·001
0·00	4·1028 ± 0·0003

The lattice parameter may be expressed as the following function of x:

$$a_0 = 0\cdot1277(1 - x) + 3\cdot9751$$

TABLE 2.—LATTICE PARAMETERS FOR THE SYSTEM $SrMo_xTi_{(1-x)}O_3$

x	a_0 (Å)
0·75	3·958
0·50	3·939
0·25	3·923
0·00	3·904[3]

The lattice parameter can be expressed as the following function of x:

$$a_0 = 0\cdot0711x + 3\cdot904$$

(d) *Electrical measurements*

The d. c. resistivities of the sintered bars of the previously described dimensions were measured by a two point probe method. A 12 V battery served as a power supply and a Type K potentiometer was used to measure the voltage drop. The estimated accuracy of the data is ±3 per cent; this relatively large uncertainty is due to errors in measuring the potential probe spacings and cross-sectional area of the sample. The reported values are characteristic only of the as-sintered bars, which usually exhibited 80 per cent of the theoretical density. At present no reliable extrapolation to correct for the residual porosity and the pore distribution is available.

The Seebeck coefficient of the various compositions was established by butting the bars between two copper blocks, one of which was cooled and the other of which was heated; e.m.f's were measured with Type K potentiometer (Leeds & Northrup). Table 3 summarizes the resistivity and Seebeck coefficient data for the investigated compounds.

[2] J. B. NELSON and D. P. RILEY, *Proc. Phys. Soc.* **57**, 160 (1945).
[3] R. S. ROTH, *J. Res. Nat. Bur. Stand.* **58**, No. 2, 78 (1957).

Fig. 1 represents a typical e.m.f. vs. ΔT plot for $SrMo_{0.75}Zr_{0.25}O_3$ as obtained in reference to copper. The lower temperature T_1 varied between 21° and 23°C. The same linear relationship was observed for all the rest of the compounds.

In the absence of evidence to the contrary, it seems reasonable to assume that $SrMoO_3$ is a metallic conductor analogous to the stoicheiometric "tungsten bronze" $NaWO_3$, with about 10^{22}

TABLE 3.—RESISTIVITY AND THERMAL E.M.F. DATA FOR VARIOUS COMPOUNDS OF THE SYSTEMS $SrMo_xZr_{(1-x)}O_3$[1] AND $SrMo_xTi_{(1-x)}O_3$[2]

x	Electrical resistivity (ohm cm)	Seebeck coefficient (μV/°C)
0·25[1]	$2{\cdot}30 \times 10^{1}$	+48·0
0·50[1]	$2{\cdot}09 \times 10^{-3}$	+5·0
0·75[1]	$6{\cdot}19 \times 10^{-4}$	+1·5
0·10[2]	$1{\cdot}02 \times 10^{2}$	+99·0
0·25[2]	1·82	+22·0
0·50[2]	$4{\cdot}01 \times 10^{-3}$	+5·0
0·75[2]	$3{\cdot}88 \times 10^{-4}$	+1·6
$SrMoO_3$	$2{\cdot}4 \times 10^{-5}$	+1·0

carriers per cm^3.[4] One would hope to increase both the carrier mobility and the Seebeck coefficient of $SrMoO_3$ by reducing the carrier density in forming the solid solutions described here, and to develop thereby materials of practical value for thermoelectric devices.[5] Actually, a proportionate variation in carrier concentrations as Mo is replaced by Ti or Zr, even if accompanied by any reason-

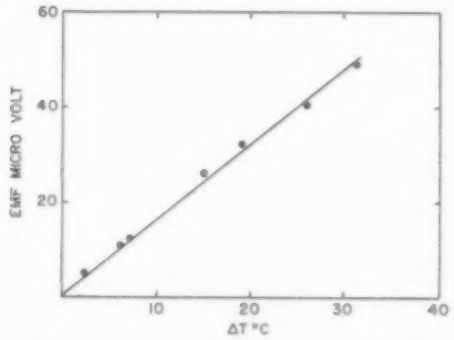

FIG. 1.—Thermal e.m.f. vs. ΔT for $SrMo_{0.75}Zr_{0.25}O_3$ ($T_1 = 22$°C).

able decrease in mobility, cannot account for the observed rapid rise of the resistivity. Hence, it may be inferred that some significant changes occur in the electronic band structure, but the available data are not adequate to define the nature of these changes.

Acknowledgement—The assistance of Mr. A. F. MATERA in determining the parameters is greatly appreciated.

[4] W. GARDNER and G. C. DANIELSON, *Phys. Rev.* **93**, 46 (1954).
[5] A. F. IOFFE and L. S. STIL'BANS, *Rep. Progr. Phys.* **22**, 167 (1959).

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 359 to 364. Pergamon Press Ltd.

THE FREE ENERGY, HEAT AND ENTROPY OF FORMATION OF THORIUM TETRAFLUORIDE*

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Abstract—The equilibrium constant for the reaction, $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$ was determined over the temperature interval 871°–1077°K by measuring the equilibrium pressure of SiF_4 above the system. The pressure of SiF_4 from this reaction is given by

$$\left[\log P_{(\text{atm})} = \frac{-8200 \pm 120}{T(°\text{K})} + 7{\cdot}740 \pm 0{\cdot}130.\right]$$

A heat capacity correction of $-2{\cdot}76$ cal deg^{-1} mole^{-1} gives for the reaction at 298°K, $\Delta F° = 27{\cdot}9$ kcal/mole, $\Delta H° = 39{\cdot}4$ kcal/mole, and $\Delta S° = 38{\cdot}7$ cal deg^{-1} mole.$^{-1}$ From these and existing thermodynamic data for SiO_2, ThO_2 and SiF_4 the $\Delta F°$, $\Delta H°$ and $\Delta S°$ of formation of ThF_4 from the elements at 298°K were calculated to be $-459{\cdot}9$ kcal/mole, $-482{\cdot}4$ kcal/mole and $-75{\cdot}8$ cal deg^{-1} mole^{-1}, respectively.

THE reaction of metal fluorides with silica has been previously noted by several workers.[1,2,3] In earlier work by the author,[4] it was observed that thorium tetrafluoride reacted with quartz at elevated temperatures to form SiF_4 gas. The present study showed that a reversible reaction occurred between thorium tetrafluoride and silica and the products, silicon tetrafluoride and thorium dioxide. The equilibrium constant was determined by measuring the pressure of SiF_4 above the system at equilibrium. The derived thermochemical constants for this reaction were combined with the published thermochemical properties of ThO_2,[5] SiO_2[5] and SiF_4[6] to obtain $\Delta F°$, $\Delta H°$ and $\Delta S°$ of formation of solid ThF_4.

EXPERIMENTAL

Materials. Thorium tetrafluoride was obtained from the A. D. Mackay Company. This material initially contained 0·2 weight per cent volatile impurities, most of which was water. The salt was purified by heating under vacuum at 600° for 16 hr to remove the volatile impurities. Analysis then showed 75·3% Th, 25·4% F (Theoretical, 75·33% Th and 24·67% F). Silicon dioxide was prepared by reacting C. P. grade silicon tetrafluoride with water. The precipitate was washed, filtered and then fired at 800°C until a constant weight was obtained. This process gave fine particles of SiO_2 powder

* This work was supported by the U.S. Atomic Energy Commission. This paper was presented in part before the Division of Physical Chemistry at the 133rd National Meeting of the American Chemical Society in April, 1958.

[1] J. W. MELLOR, *Comprehensive Treatise of Inorganic and Theoretical Chemistry*. Longmans, Green, London (1952).
[2] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium*. McGraw-Hill, New York (1951).
[3] M. V. SMIRNOV and L. E. IVANOWSKII, *Zh. Neorg. Khim.* **1**, 1843 (1956).
[4] A. J. DARNELL and F. J. KENESHEA, JR., *J. Phys. Chem.* **68**, 1143 (1958).
[5] J. P. COUGHLIN, U.S. Bureau of Mines Bull. 542 (1954).
[6] L. L. QUILL, *Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics*. McGraw-Hill, New York (1950).

which reacted more rapidly with ThF_4 than commercially available SiO_2. Thorium dioxide of 99·8 per cent purity was obtained from Rare Earths Incorporated; it was heated *in vacuo* at 700°C for a period of 16 hr before use.

Samples for the equilibrium studies were prepared by thoroughly mixing together equimolar quantities of powdered ThF_4 and SiO_2, then compressing this mixture into pellets with a hydraulic press at a pressure of 2 tons/in². These pellets were then broken into approximately 1 mm cubes. Mixtures prepared in this manner reacted satisfactorily to give equilibrium pressures of SiF_4 in from 2 to 4 hr. Less thorough mixing resulted in slower reaction rates which required from 1 to 5 days to attain equilibrium.

Apparatus and procedure

The pressure of SiF_4 above the solid reactants was measured using the manometric technique. The solid reaction mixture, ThF_4 and SiO_2, was placed in a quartz reaction cell surrounded by a nickel thermal shield to minimize thermal gradients. This assembly was placed in a tube furnace maintained at a constant temperature (±2°C) by a potentiometric type regulator. The temperature of the reaction was measured by a calibrated Pt-Pt 90 per cent, Rh 10 per cent thermocouple placed in a well in the quartz cell. The reaction cell was connected to a mercury manometer by a 6 mm quartz tube packed with quartz wool to reduce thermal convection in the system. This apparatus was connected to a vacuum system, gas sampling bulb, and inlet for introducing SiF_4 into the cell.

Measurements of SiF_4 equilibrium pressures were made by the following procedures: The system was evacuated at room temperature, then at 400°C for 1 hr to remove adsorbed impurities. The system was then sealed off from the vacuum pump, the reaction cell was raised to the desired temperature and the pressure of SiF_4 measured by means of the mercury manometer. Pressure readings were taken until there was no further change in pressure with time.

RESULTS AND DISCUSSION

Equilibrium pressures of SiF_4 obtained from the reaction of ThF_4 and SiO_2 are shown in Table 1.

SiF_4 was identified as the gaseous product of the reaction by chemical and mass spectrographic analysis of gas samples taken from the reaction cell. Room temperature X-ray diffraction analyses of samples quenched from equilibrium, in which 70 mole per cent of the fluorine had been converted to SiF_4, showed that the major solid product was thorium dioxide.[7] Under forcing conditions, i.e. by removal of SiF_4 by condensation on a cold finger, equimolar amounts of ThF_4 and SiO_2 reacted essentially quantitatively (>99 per cent) to ThO_2 and SiF_4. The overall reaction can thus be represented by

$$ThF_4(s) + SiO_2(s) = ThO_2(s) + SiF_4(g). \quad (1)$$

Further studies were made to determine if reaction (1) represents the solid phases in the equilibrium since the X-ray diffraction patterns of quenched samples showed traces of thorium oxyfluoride.[8] D'EYE[8] reports that ThF_4 and ThO_2 react at 900–1000°C to form $ThOF_2$. Tests carried out on the reverse of reaction (1), by reacting SiF_4 with pure ThO_2, yielded equilibrium pressures which were in good agreement with those obtained from the forward reaction (see Table 2). This indicated that the phases in the equilibrium were as shown in reaction (1). In addition, reaction of $ThOF_2$* and SiO_2 gave equilibrium pressures of SiF_4 which were lower than the pressures yielded by the reaction of ThF_4 and SiO_2.

* $ThOF_2$ prepared by method of D'EYE[8].

[7] H. E. SWANSON and E. TATGE, *Standard X-ray Diffraction Patterns*. National Bureau of Standards Circ. 539. Vol. 1. p. 57 (1953).
[8] R. W. M. D'EYE, *J. Chem. Soc.* 196 (1958).

Vol. 15 1960

The solid solution of ThF_4 in ThO_2, to the extent of 25 mole per cent ThF_4 at 1000°C, found by D'Eye[8] probably does not occur to an appreciable extent at the lower temperatures of this investigation since the equilibrium pressures of SiF_4 from reaction (1) and from the reverse of reaction (1) were essentially constant (at constant temperature) over the entire composition range. Therefore, the activities of the solid phases

Table 1.—Equilibrium pressures of SiF_4 for the reaction

$$ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$$

Temperature (°K)	P_{SiF_4} (atm)
Equilibrium approached from lower pressures	
871	0·020
882	0·034
886	0·026
935	0·085
937	0·097
945	0·114
960	0·154
985	0·245
995	0·290
1000	0·318
1038	0·651
1076	1·289
1077	1·260
Equilibrium approached from higher pressures	
884	0·038
936	0·094
1030	0·660
1054	1·200

Table 2.—Equilibrium pressures of SiF_4 for the reaction

$$SiF_4(g) + ThO_2 \rightleftharpoons ThF_4(s) + SiO_2(s)$$

Temperature (°K)	P_{SiF_4} (atm)
923	0·073
1043	0·659

were apparently the same whether the solid phases ThO_2 and ThF_4 or SiO_2 were in excess.

The agreement of the final pressures of SiF_4, when approached from zero pressure and from pressures above the equilibrium pressure offers good evidence that chemical equilibrium was attained. Fig. 1 shows the pressure of SiF_4 vs. time for reaction (1), starting from zero pressure and from 0·2 atm SiF_4. Similar experiments were carried out at 884°, 1030° and 1054°K; the results are shown in Table 1 and Fig. 2.

The activities of the solid phases in reaction (1) were considered to be unity for the following thermodynamic calculations. Assuming SiF_4 behaves as an ideal gas, the equilibrium constant for reaction (1) may be expressed as,

$$K = P_{SiF_4} \tag{2}$$

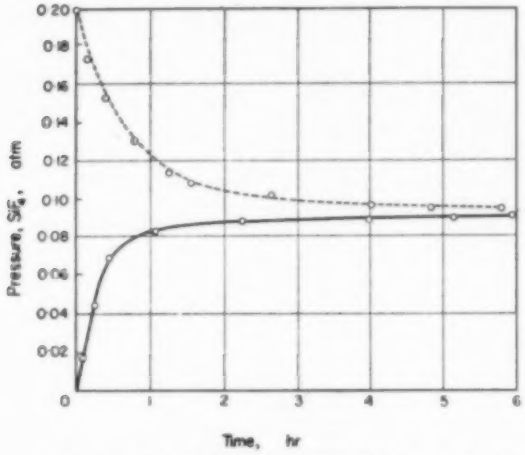

FIG. 1.—Pressure of SiF_4 vs time at 936° for the reaction: $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(g) + SiF_4(g)$.

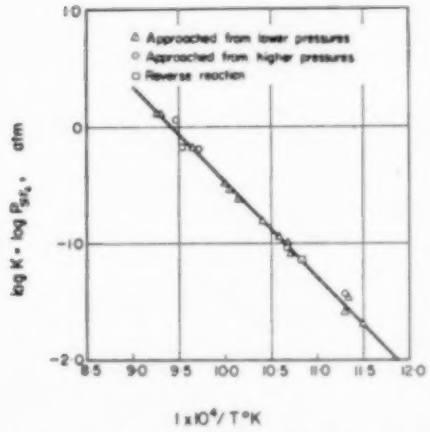

FIG. 2.—Equilibrium constant vs $1/T$ for the reaction: $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$.

A least squares analysis was made of the P_{SiF_4} data in Tables 1 and 2. The pressure of SiF_4 as a function of temperature is:

$$\log P_{SiF_4}\,(\text{atm}) = \frac{-8200 \pm 120}{T°\text{K}} + 7{\cdot}740 \pm 0{\cdot}130,\ (871\text{–}1077°\text{K}), \tag{3}$$

The enthalpy of the reaction is obtained from the van't Hoff equation. At the mid-temperature of the experimental range (974°K), $\Delta H°$ (reaction) $= +37{\cdot}5 \pm 0{\cdot}5$

Vol. 15 1960

kcal/mole. The ΔC_p of reaction (1) is $-2{\cdot}76$ cal deg^{-1} mole^{-1} at 298°K (see Table 3). It is assumed that ΔC_p is constant from 298 to 974°K, since there are no high temperature heat capacity data for ThF_4. Then ΔF_T° for reaction (1) is:

$$\Delta F_T^\circ = 40{,}210 + 6{\cdot}36T \log T - 57{\cdot}19T \tag{4}$$

The following results are calculated for the reaction at 298°K:

$$\Delta F^\circ = 27{\cdot}9 \text{ kcal mole}^{-1} \tag{5}$$

$$\Delta H^\circ = 39{\cdot}4 \text{ kcal mole}^{-1} \tag{6}$$

$$\Delta S^\circ = 38{\cdot}7 \text{ cal deg}^{-1} \text{ mole}^{-1} \tag{7}$$

The above data were combined with published thermochemical data for $ThO_2(s)$,

TABLE 3.—THERMODYNAMIC DATA

	$\Delta H^\circ_{298}(f)$ $\left(\frac{\text{kcal}}{\text{mole}}\right)$	$\Delta F^\circ_{298}(f)$ $\left(\frac{\text{kcal}}{\text{mole}}\right)$	$\Delta S^\circ_{298}(f)$ $\left(\frac{\text{cal}}{\text{deg-mole}}\right)$	S°_{298} $\left(\frac{\text{cal}}{\text{deg-mole}}\right)$	C°_{p298} $\left(\frac{\text{cal}}{\text{deg-mole}}\right)$
$ThO_2(s)$	$-293{\cdot}2 \pm 0{\cdot}4$[5]	$-279{\cdot}2$[5]	$-47{\cdot}0$	—	$14{\cdot}76$[11]
$SiF_4(g)$	$-359{\cdot}7 \pm 2{\cdot}8$[12]	$-349{\cdot}7$	$-33{\cdot}7$	$67{\cdot}77$[12]	$17{\cdot}56$[12]
SiO_2(α-quartz)	$-209{\cdot}9 \pm 1{\cdot}0$[5]	$-196{\cdot}9$[5]	$-43{\cdot}6$	—	$10{\cdot}62$[14]
Reaction: $ThF_4(s) + SiO_2(\text{quartz}) = ThO_2(s) + SiF_4(g)$					
	$39{\cdot}4 \pm 0{\cdot}5$*	$27{\cdot}9$*	38·7K	—	$\Delta C_p = -2{\cdot}76$
$ThF(s)$	$-482{\cdot}4 \pm 3{\cdot}5$*	$-459{\cdot}9$*	$-75{\cdot}8$*	$33{\cdot}9$*	—
$ThF_4(s)$	-477[6]	-454[6]	-76[6]	(estimate by L. BREWER)	
$Th(s)$	—	—	—	$12{\cdot}76$[9]	—
$2F_2(g)$	—	—	—	$96{\cdot}90$[9]	—
$ThF_4(s)$	—	—	—	$33{\cdot}9$[10]	$26{\cdot}46$[10]

* This work.

$SiO_2(s)$ and $SiF_4(g)$ (Table 3), to obtain the free energy, enthalpy and entropy of formation of ThF_4(s) from the elements in their standard states at 298°K. This yields

$$\Delta F^\circ = -459{\cdot}9 \text{ kcal mole}^{-1} \tag{8}$$

$$\Delta H^\circ = -482{\cdot}4 \text{ kcal mole}^{-1} \tag{9}$$

$$\Delta S^\circ = -75{\cdot}8 \text{ cal deg}^{-1} \text{ mole}^{-1} \tag{10}$$

The absolute entropy of $ThF_4(s)$, obtained from the above ΔS°_{298} of formation of

[9] D. R. STULL and G. C. SINKE, *Thermodynamic Properties of the Elements*. American Chemical Society, Washington (1956).
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[14] C. T. ANDERSON, *J. Amer. Chem. Soc.* **58**, 568 (1936).

$ThF_4(s)$ and S°_{298} of $Th(s)$[9] and $F_2(g)$[9] (see Table 3), is 33·9 cal deg^{-1} $mole^{-1}$. LOHR *et al.*[10] report $S^\circ_{298} = 33{\cdot}9$ cal deg^{-1} $mole^{-1}$ from low temperature heat capacity measurements on thorium tetrafluoride.

It is pointed out that this equilibrium method inherently has the combined uncertainties of the thermodynamic properties of ThO_2, SiO_2 and SiF_4 in addition to the uncertainty of this measurement. The uncertainty in ΔH°_{298} (ThF_4) is estimated to be $\pm 3{\cdot}5$ kcal/mole.

The equilibrium between a metal oxide and metal fluoride offers a convenient method for determining the thermodynamic properties of a metal fluoride which is not amenable to measurements by calorimetric or electromotive force methods.

Acknowledgements—The author wishes to express appreciation to Dr. S. J. YOSIM and Dr. D. E. MCKENZIE for many helpful discussions and to Mr. W. A. MCCOLLUM for assistance in carrying out the experimental work.

Vol.
15
1960

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AN INFRA-RED STUDY OF THE SYSTEMS TRI-N-BUTYL PHOSPHATE–HNO_3 AND BIS-(2-ETHYLHEXYL)-PHOSPHORIC ACID–HNO_3*

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Abstract—An infra-red study of the systems tri-n-butyl phosphate†–HNO_3 and bis-(2-ethylhexyl)-phosphoric acid‡–HNO_3 has been made. It has been observed that the nitric acid extracting into these organophosphorus solvents is predominantly of a molecular nature, and that the bonding is primarily to the phosphoryl oxygen. In the TBP system, at low HNO_3 concentrations and high aqueous content, some contribution from ionized HNO_3 species is possible. The distribution coefficients of HNO_3 for these systems are also reported.

THE extraction of various cations into TBP and HDEHP from aqueous HNO_3 solutions has been extensively investigated.[1–8] It has been known that HNO_3 will extract readily into TBP.[9–10] The solvent HDEHP has also been shown to extract HNO_3.[7] However, the nature of the HNO_3 in the complexes TBP–HNO_3 and HDEHP–HNO_3 has never been elucidated. This paper reports on an infra-red investigation concerning the nature of the HNO_3 in these complexes.

EXPERIMENTAL

TBP (Eastman Kodak Co.) and purified HDEHP (Victor Chem. Wks.) were contacted in equal volume portions one or more times with solutions of HNO_3 of various concentrations, including 100% HNO_3. The mixtures were shaken for 3 min or longer, centrifuged and the organic phase separated from the aqueous phase. A weighed aliquot of the organic phase was water-washed three to four times to remove the HNO_3. The water wash solutions were combined and titrated for HNO_3 by standard alkali titration using phenolphthalein as the indicator. Water determinations of separate weighed aliquots of the organic phase were made by Karl Fischer titration.[11] For infra-red investigation, the HNO_3-containing organic phase, after separation from the aqueous phase, was placed in a cell with AgCl windows, and the spectrum determined with a Model No. 21 Perkin–Elmer spectrophotometer. The spectrum of 100% HNO_3 was also determined in this manner.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission. Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 1960.

† Henceforth abbreviated TBP.

‡ Henceforth abbreviated HDEHP.

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D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).
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DISCUSSION AND RESULTS

System TBP–HNO_3–H_2O

A. *Distribution coefficient of* HNO_3 *in* TBP. The distribution data for the extraction of HNO_3 in TBP are presented in Table 1. The results substantiate those of MCKAY and co-workers.[8] With increasing extraction of HNO_3 into the TBP phase, the ratio $[{}_mH_2O/{}_mTBP]_{org}$ decreases to a minimum, then appears to increase, but never reaches the value attained in aqueous saturated TBP containing no HNO_3.

TABLE 1.—SYSTEM TBP–HNO_3–H_2O

Equilibrated organic phase						Equilibrated aqueous phase	
${}_mHNO_3$	${}_mH_2O$	${}_mTBP$	$\left[\frac{{}_mHNO_3}{{}_mTBP}\right]$	$\left[\frac{{}_mH_2O}{{}_mTBP}\right]$	$\left[\frac{{}_mH_2O}{{}_mHNO_3}\right]$	${}_mHNO_3$	K_d*HNO_3
0·47	3·49	3·41	0·14	1·02	7·43	0·53	0·89
1·60	3·14	3·16	0·51	0·99	1·96	2·13	0·75
2·41	2·64	3·01	0·80	0·88	1·10	3·83	0·63
2·80	1·60	2·98	0·94	0·54	0·57	4·83	0·58
3·10	1·50	2·92	1·06	0·51	0·48	5·64	0·55
3·62	1·44	2·80	1·29	0·51	0·40	7·39	0·49
3·67	1·04	2·82	1·30	0·37	0·28	7·81	0·47
4·54	1·26	2·60	1·75	0·49	0·28	9·66	0·47
5·40	2·08	2·38	2·30	0·87	0·39	9·82	0·55
9·14	0·19(?)	1·58	5·78	—	—	one phase	one phase

* K_d is defined as the ratio of the nitric acid concentration in the organic phase divided by the nitric acid concentration in the aqueous phase; all concentrations (m) are in molal units.

The organic phase contacted with 100% HNO_3 shows a low water to TBP ratio, but results of the Karl Fischer titration in the presence of very strong acids are not considered dependable, even if pyridine is added in the titration.[11] The nitric acid to TBP ratio increases steadily to a maximum at 5·78, while the water to HNO_3 ratio decreases to an apparent minimum. The distribution coefficients decrease to a minimum, with increasing aqueous HNO_3 concentration; then appear to increase until one phase is obtained with 100% HNO_3. The acid can be scrubbed out from the TBP with water, and the infra-red spectrum of the TBP is identical to the spectrum of the TBP–H_2O compound, showing that the TBP is recovered unchanged.

B. *Infra-red study.* In analysing the infra-red spectra of the TBP–HNO_3 and HDEHP–HNO_3 complexes it is of interest to discuss the results of the infra-red spectrum of HNO_3.[12–14] The configuration of nitric acid corresponds to C_s symmetry.[13] If the hydroxyl group is considered as a single unit (rigid), then the symmetry becomes that of C_{2v}. The absorption frequencies expected for the C_{2v} type of

[12] R. A. MARCUS and J. M. FRESCO, *J. Chem. Phys.* **27**, 564 (1957).
[13] G. HERZBERG, *Infra-red and Raman Spectra of Polyatomic Molecules* p. 322. Van Nostrand, New York (1945).

Vol. 15 1960

symmetry in HNO_3 have been discussed.[14–18] Four important absorption bands are found in the infra-red spectrum of 100% HNO_3 at 1680, 1308, 924 and 769 cm^{-1}. These absorptions are attributed to molecular HNO_3.[13–16] A shoulder appears at about 1420 cm^{-1} and this has been attributed by INGOLD[15] to NO_2^+ absorption from the self-ionization of HNO_3. The bonded OH stretching absorption occurs at 3300 cm^{-1}.[13–16] Addition of water to 100% HNO_3 causes the appearance of bands at 828 and 1380–1410 cm^{-1} which have been attributed to the nitrate ion.[13–16] These

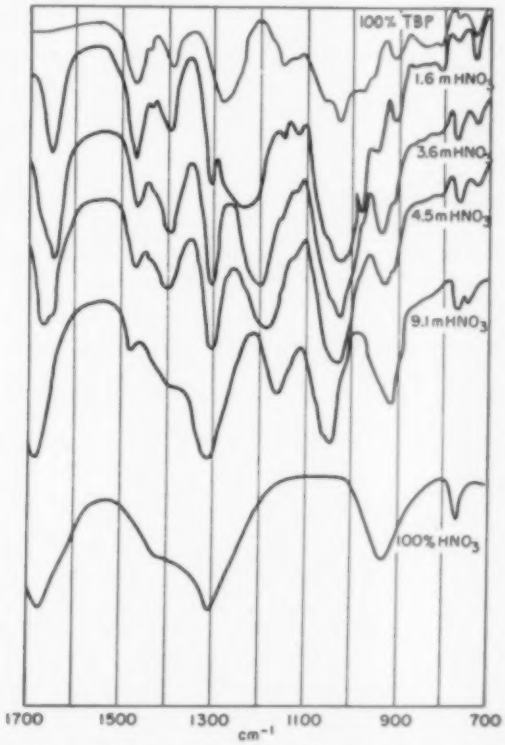

FIG. 1.—Infra-red absorption spectra of TBP–HNO_3 complex (extraction experiments).

are the regions of interest in studying the spectra of the TBP–HNO_3 and HDEHP–HNO_3 complexes.

The infra-red spectra from 700 to 1700 cm^{-1} at various concentrations of HNO_3 in TBP are shown in Fig. 1. These results are obtained by extraction from an aqueous HNO_3 solution into TBP. It has been observed that as the HNO_3 concentration increases, peaks in the regions at about 775, 925, 1300, 1675 and 3300 cm^{-1} all increase. The P → 0 peak, which in pure TBP is at about 1280 cm^{-1} (actually a doublet),[17] has shifted toward a lower frequency and at about nine molal HNO_3 is

[14] D. REDLICH and L. E. NIELSEN, *J. Amer. Chem. Soc.* **65**, 654 (1943).
[15] C. K. INGOLD and D. J. MILLEN, *J. Chem. Soc.* 2612 (1950).
[16] R. A. ROBINSON and R. H. STOKES, *Electrolyte Solutions*. Academic Press, New York (1959).
[17] F. S. MORTIMER, *Spectrochimica Acta* **9**, 270 (1957).
[18] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, New York (1958).

near 1150 cm^{-1}, representing a shift of approximately 130 cm^{-1}. The broad bonded [P]-OH regions,[18-19] near 2300 cm^{-1} and 2700 cm^{-1} also appear. The region at about 1700 cm^{-1}, and attributed to the [P]-OH deformation,[19,20] is masked because of the HNO_3 absorption. The region at 1400 cm^{-1} appears to increase slightly at the outset. This is, probably, due to the presence of NO_3^-, but at higher concentrations of HNO_3 the absorption in this region is also due to the nitronium ion, NO_2^+. The region at 800 cm^{-1} shows little change with the addition of HNO_3. It is concluded that HNO_3 extracts into the TBP organic phase predominantly as molecular HNO_3.

TABLE 2.—SYSTEM HDEHP–HNO_3–H_2O

Equilibrated organic phase						Equilibrated aqueous phase	K_d*HNO_3
$_mHNO_3$	$_m$HDEHP	$_mH_2O$	$\left[\frac{_mHNO_3}{_m\text{HDEHP}}\right]$	$\left[\frac{_mH_2O}{_m\text{HDEHP}}\right]$	$\left[\frac{_mH_2O}{_mHNO_3}\right]$	$_mHNO_3$	
0·63	2·84	1·80	0·22	0·63	2·86	3·69	0·17
0·79	2·83	1·50	0·28	0·53	1·90	5·82	0·14
1·86	2·64	1·10	0·71	0·42	0·59	9·74	0·19
2·61	2·49	1·15	1·06	0·46	0·44	10·10	0·26
3·55	2·34	1·15	1·52	0·49	0·32	11·19	0·32
8·11	1·48	0·51	5·48	0·34	0·06	14·15	0·57
10·98	0·95	nil(?)	11·55	—	—	15·63	0·70

* K_d is defined as the ratio of the nitric acid concentration in the organic phase divided by the nitric acid concentration in the aqueous phase; all concentrations (m) are in molal units.

The bonding at low HNO_3 concentration is considered to be chiefly $(BuO)_3P \rightarrow O \ldots . HNO_3$, with some contribution from ion pairs. In view of the fact that the bonded [P]-OH regions are so strongly manifested, even at low concentrations of HNO_3 in the organic phase, the $(BuO)_3P \rightarrow O \ldots . H^+$ ion must represent only a small fraction of the total HNO_3 present.[10] At present the possibility that some of the excess HNO_3 binds to itself or to the ester oxygen in TBP cannot be definitely evaluated. The region at about 1040 cm^{-1}, which is attributed at least in part to the [P-O]-C stretching vibration, does broaden and intensify slightly with the addition of HNO_3.

System HDEHP–HNO_3–H_2O

A. *Distribution coefficient of* HNO_3 *in* HDEHP. The data for the extractions of HNO_3 into HDEHP are shown in Table 2. The $[_mH_2O/_m\text{HDEHP}]_{org}$ ratio, which is 0·33 in a phase equilibrated against water, is 0·63 for the system involving the lowest HNO_3 content studied and thereafter decreases; although again it should be noted that in strong acid, data for water content are questionable. The water/solvent ratio in this system appears, in general, to be smaller than in the TBP–HNO_3–H_2O

[19] L. C. THOMAS, *Chem & Ind.* 197 (1957).
[20] J. W. MAARSEN, M. C. SMIT and J. MATZE, *Rec. Trav. Chim.* **76**, 713 (1957).

system, being one-third as large in the absence of HNO_3. The nitric acid to HDEHP ratio increases to a maximum at 11·6, while the water to HNO_3 ratio shows a steady decrease. The distribution coefficient (K_d) of HNO_3 appears to be fairly constant at about 0·15 until an aqueous HNO_3 concentration of about 10 molal is reached, above which the K_d increases sharply, rising to 0·70 at 15·6 molal aqueous HNO_3. The HDEHP can be recovered from the mixed HDEHP–HNO_3 solutions unchanged, as shown by its infra-red spectrum.

B. *Infra-red study*. Table 2 illustrates the infra-red spectrum of the complex

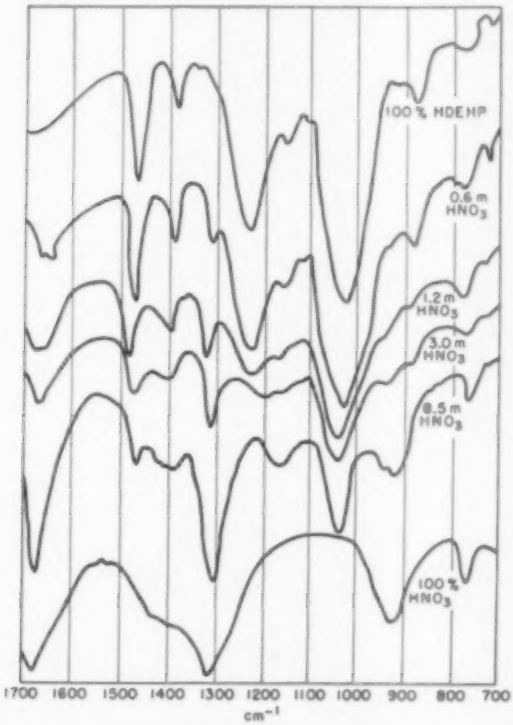

FIG. 2.—Infra-red absorption spectra of HDEHP–HNO_3 complex (extraction experiments)

HDEHP–HNO_3 in the region 700–1700 cm^{-1}. The molecular HNO_3 regions at 1675, 1300, 925 and 775 cm^{-1} appear as soon as HNO_3 extracts into the HDEHP phase. The P → O frequency shifts from 1225 cm^{-1} in pure HDEHP to 1158 cm^{-1} at about 11 molal HNO_3. The exact nature of the bonding to the P → O is still open to question. It is uncertain if a new hetero-dimer is formed, or whether the HNO_3 simply forms a new hydrogen bond to one of the oxygens of the dimer. In view of the large shift in the P → O frequency, it is believed that the dimer $(HDEHP)_2$ is broken, and a new hydrogen bond to the P → O forms with the hydrogen of the HNO_3. However, after high HNO_3/HDEHP ratios are reached, the concept of bonding to HDEHP is meaningless. The region 2350–2700 cm^{-1}, which in $(HDEHP)_2$ is attributed to the bonded [P]-OH stretching motion, appears to be maintained with the addition of HNO_3. This would be expected, since, even if the $(HDEHP)_2$ dimer is broken new

bonds with the hydrogen of the HNO_3 would give rise to a bonded [P]-OH absorption in the same approximate region. In the 3 μ region a broad absorption band builds up at 3250 cm^{-1} at the first addition of HNO_3. This may be compared with the band observed at 3300 cm^{-1} for anhydrous HNO_3. It would thus appear that as the HNO_3, extracts into the HDEHP phase it extracts as molecular HNO_3, much as it does into TBP. However, since the regions at 1400 and 800 cm^1 show only weak intensities upon addition of HNO_3, it is believed that the NO_3^- concentration at the outset is much smaller in the HDEHP–HNO_3 system than it is in the TBP–HNO_3 system. As in the case of TBP the region at about 1040 cm^{-1} broadens with the further addition of HNO_3. Some HNO_3—HNO_3 bonding is possible, although not definitely proven.

Systems TBP–HCl–H_2O *and* HDEHP–HCl–H_2O

The limited amount of HCl extracted into TBP and HDEHP prevented an infra-red study of these complexes. In the TBP system the K_d of HCl reaches a value of only 0·39 at 8 molal aqueous HCl. In the HDEHP the K_d value is 0·16 at 10 molal aqueous HCl.

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Vol. 15 1960

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THE KINETICS OF THE REDUCTION OF PERMANGANATE BY CYANIDE IN BASIC SOLUTION

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Abstract—Permanganate is reduced by cyanide quantitatively in basic aqueous solution according to the equation: $2MnO_4^- + CN^- + 2OH^- = 2MnO_4^{2-} + CNO^- + H_2O$. In the region of 0·07 M OH^- the kinetics follow the rate law: $-d(MnO_4^-)/dt = k[MnO_4^-][CN^-]$ with $k = 6{\cdot}4 \times 10^7 \exp(-9000/RT)$ l/mole sec. At higher $[OH^-]$ the rate depends on $[OH^-]$ and a reaction path involving $OH\cdot$ may play a role.

$KMnO_4$ is one of the most widely used oxidizing agents. Mechanisms of oxidations by $KMnO_4$ have been studied by isotopic tracers and by rate measurements and these have been recently reviewed.[1,2] For oxidations yielding MnO_4^{2-} the prime interest has been in organic reductants. Very little is known about the kinetic behaviour of permanganate with respect to common inorganic reducing agents. This paper is the first in a series of redox studies using higher valent manganese oxy-anions.

With inorganic reducing agents, only two kinetic studies have been made in basic solution involving MnO_4^- in which the reaction stops at MnO_4^{2-}. With H_2 as the reducing agent[3] the rate of disappearance of MnO_4^- has a frequency factor $8{\cdot}4 \times 10^9$ l/mole sec and an activation energy of 14·7 kcal. SHEPPARD and WAHL[4] have estimated the second order rate constant for the reduction of MnO_4^{2-} by hexacyanoferrate (II) to be 10^4 l/mole sec at 0°C. Their estimate was based on the catalysis of the manganate–permanganate electron exchange reaction by hexacyanoferrate (III) ion. Also, SYMONS[5] has studied the rate of the spontaneous decomposition of MnO_4^- in alkali with the production of O_2 and manganate. He found the course of the reaction followed complex kinetics.

Stoicheiometric reductions of MnO_4^- to MnO_4^{2-} have been found[6] for iodide, iodate, formate, arsenite and cyanide all in basic solution in the presence of barium ion. (Barium forms an insoluble manganate.) DRUMMOND and WATERS comment that the cyanide reaction is rapid. In the absence of barium ion it has been shown[7] that CN^- does not reduce MnO_4^{2-}.

EXPERIMENTAL

The rate of the reaction was followed on a Beckman DK1 spectrophotometer using 0·5, 1·0, 5·00, 10·0 cm cells which were thermostatted to within 0·2°C. All glassware was cleaned first with an oxalic–hydrochloric acid solution followed by rinsing with redistilled water, next washed with chromic acid cleaning solution, and finally, repeatedly rinsed with redistilled water. All solutions

[1] J. W. LADBURY and C. F. CULLIS *Chem. Rev.* **58**, 403 (1958).
[2] W. A. WATERS, *Quart. Rev.* **12**, 277 (1958).
[3] A. WEBSTER, J. HALPERN, *Trans. Faraday Soc.* **53**, 51 (1957).
[4] J. C. SHEPPARD and A. C. WAHL, *J. Amer. Chem. Soc.* **79**, 1020 (1957).
[5] M. C. R. SYMONS, *J. Chem. Soc.* 3956 (1953).
[6] A. Y. DRUMMOND and W. A. WATERS, *J. Chem. Soc.* 435 (1953).
[7] J. S. F. PODE and W. A. WATERS, *J. Chem. Soc.* 717 (1956).

were prepared from redistilled water, which had been made in a two stage still, the first stage containing concentrated $KMnO_4$ in alkali. The KCN solutions were freshly prepared in base (low in CO_3^{2-}) from a single bottle of A.C.S. Reagent KCN which was found to be better than 99 per cent pure by titration with silver nitrate. The molarity of the KCN solutions was based on the amount of KCN weighed out. The $KMnO_4$ solutions were freshly prepared from two different stock 0·02 M $KMnO_4$ solutions by dilution with redistilled water. The $KMnO_4$ solutions for each run were assayed by titration with excess iodide.

The other chemicals except K_2MnO_4, which was prepared in our laboratory, were A.C.S. Reagent grade and used without further purification.

Most kinetic measurements were made at 530 mμ at a slit width of 0·28 mm and a few measurements were made at 610 mμ at a slit width of 0·15 mm. For each run a blank was prepared from the same solutions except that the KCN was omitted from the caustic solution. For 0·07 M base the decomposition of the $KMnO_4$ in the blank was negligible.

The molar extinction coefficients of $KMnO_4$ and K_2MnO_4 were found to be temperature independent from 5 to 40°C. The molar extinction coefficients for K_2MnO_4 were determined by reducing a known amount of $KMnO_4$ in basic solution with KCN. Ten solutions with mole ratios of CN^-/MnO_4^- from 0 to 1 were measured over a period of 12 hr. After about 6 hr the molar extinction coefficients of the solutions with mole ratios of 0·45–1·0 were identical within experimental error for 530 mμ and 610 mμ. The molar extinction coefficients found for MnO_4^- were 2185 and 223 and for MnO_4^{2-} were 395 and 1347 at 530 mμ and 610 mμ respectively.

It was determined that there was no photochemical effect due to the irradiation of the sample while in the spectrophotometer.

EXPERIMENTAL RESULTS

The experimental data are treated by the method outlined below. Since the initial concentrations of both CN^- and MnO_4^- were known, the concentrations of CN^-, CNO^-, MnO_4^- and MnO_4^{2-} at any time (t) can be expressed as a function of the initial concentrations $[CN_i^-]$ and $[MnO_{4i}^-]$, the optical density (D), the molar extinction coefficients for MnO_4^- (ε_1) and MnO_4^{2-} (ε_2), and the light path length of the cell in cm (l).

For the case with only MnO_4^- and CN^- present initially:

$$[MnO_4^-] = \frac{D - l\varepsilon_2 b}{l(\varepsilon_1 - \varepsilon_2)} \text{ and } [CN^-] = \frac{D - l\alpha}{2l(\varepsilon_1 - \varepsilon_2)}$$

where $$\alpha = b\varepsilon_1 - 2(\varepsilon_1 - \varepsilon_2)\,[CN_i^-] \text{ and } b = [MnO_{4i}^-].$$

The rate expression $-d[MnO_4^-]/dt = k\,[MnO_4^-]\,[CN^-]$ can therefore be expressed in terms of the experimental variable optical density:

$$k = \frac{4{\cdot}606}{[MnO_{4i}^-] - 2[CN_i^-]} \cdot \frac{d \log_{10} \langle (D - lb\varepsilon_2)/(D - l\alpha) \rangle}{dt}$$

The second order rate constant was evaluated from the slope of a plot of $\log \langle (D - lb\varepsilon_2)/(D - l\alpha) \rangle$ vs. t. In cases when the difference between $[MnO_{4i}^-]$ and $2[CN_i^-]$ is small $k = 2l(\varepsilon_1 - \varepsilon_2)d\,[1/(D - lb\varepsilon_2)]/dt$. These cases were also evaluated graphically.

Fig. 1 illustrates a typical experiment. In most cases the optical density was recorded for 80 per cent of the course of each reaction. In this figure two curves are shown; curve A, the experimentally recorded values of optical density vs. time, curve B, the calculated values of $\log [(D - l\alpha)/(D - lb\varepsilon_2)]$ vs. time. Neither curve was smoothed. It is evident that curve B is very nearly a straight line. No systematic deviation from a straight line in the various experiments was observed. Thus, there

Vol. 15 1960

was no evidence that the reaction occurs in more than one kinetic stage. The specific rate constant was calculated from the slope of curve *B*.

Approximately a twenty-five-fold range of initial concentrations for both CN^- and MnO_4^- was investigated. Since each run was followed to 80 per cent completion it can be considered that a 100-fold range of concentrations has been investigated for both CN^- and MnO_4^-.

Specific rates constants for the individual experimental runs are presented in Table 1. The rate constant measurements should be expected to be reproducible to

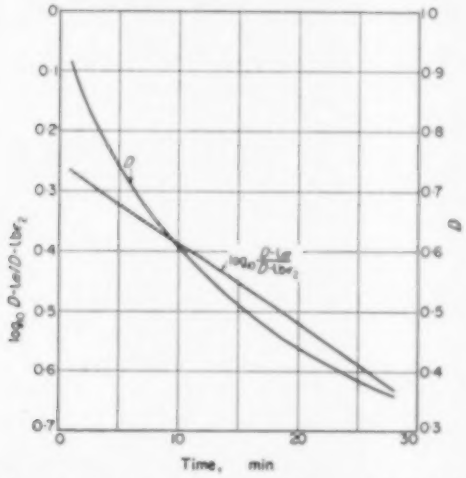

FIG. 1—One typical experiment. Curve *A*: recorded curve of optical density (*D*) vs. time in minutes. Curve *B*: Calculated (no smoothing) curve of $\log_{10}\frac{D-l\alpha}{D-lb\epsilon_2}$ vs. time in minutes; the specific constant is calculated from the slope of curve *B*.

about ± 10 per cent based on an estimate of the errors of the values of initial concentrations, molar extinction coefficients, and optical densities. The agreement among the values of the rate constants for individual runs which are listed in Table 1 is of this expected magnitude. The runs are not ordered in chronological sequence but according to increasing $[OH^-]$, second according to increasing $[MnO_4^-]$, and third according to increasing $[CN^-]$. This table illustrates the following points:

(1) substitution of K^+ for Na^+ as the principal cation has no effect (compare runs H and Q),

(2) MnO_4^{2-} and CNO^- have a very small if any inhibitory effect (see runs K and L),

(3) in the region of 0·07 M OH^- the rate is essentially independent of OH^- (runs A and R agree with runs at 0·07M), at 0·5 M OH^- a hydroxide ion path is important (see k_{OH^-} for runs S),

(4) there is no evidence for an optically absorbing species other than MnO_4^- and MnO_4^{2-} (see runs D at 530 mμ and E at 610 mμ),

(5) cyanide ion concentrations both below and above stoicheiometry have been studied (for example, a comparison of runs D and C shows that a 100 per cent excess of CN^- does not affect the rate constant).

TABLE 1.—TYPICAL EXPERIMENTS

Run No.	OH^- (mmole)	Initial conc. (mmole)		Temp. (°C)	(mmole) Initial conc.	k(l/mole sec)
		MnO_4	CN^-			
A	35	0·10	0·10	26		2·5
B	75	0·043	0·015	26		2·7
C	75	0.10	0·051	26		2·6
D	75	0·10	0·10	26		2·7
E	75	0·10	0·10	26	†	2·5
F	75	0·41	0·21	2		·74
G	75	0·41	0·20	20		2·7
H	75	0·42	0·20	26		2·5
I	75	0·47	0·21	26		2·6
J	73	0·42	0·19	27		2·3
K	75	0·48	0·21	26	0·71 MnO_4^{2-}	2·3
L	75	0·42	0·20	26	4·8 CNO^-	2·2
M	73	0·42	0·19	32		2·7
N	75	0·41	0·19	40		5·0
O	73	0·42	0·38	28		2·8
P	75	0·95	0·38	27		2·4
Q	*76	0·41	0·19	26		2·3
R	*180	0·41	0·19	26		2·8
S	*460	0·41	0·19	26	‡	3·6–5·5

* Runs with KOH instead of NaOH.
† Run E measured at 610 mμ, rest at 530 mμ.
‡ $\frac{-d\,MnO_4^-}{dt} = MnO_4^-\{k_{CN}[CN^-] + k_{OH}[OH^-] + k_d\}$ where k_d was determined from the blank. k_{OH} is estimated to be 3×10^{-4}.

From the temperature dependence of the second-order rate constant determined at 0·07 M OH^-, the activation energy was found to be 9·0 kcal and the frequency factor $6·4 \times 10^7$ l/mole sec.

In some continuing preliminary qualitative experiments we have also measured the rate of reduction of MnO_4^- to MnO_4^{2-} by other anions. With the fastest rate first, we found the order to be: Fe $[CN_6]^{4-}$, BH_4^-, $S_2O_3^{2-}$, $H_2PO_2^-$, I^-, CNS^- and $HCOO^-$.

DISCUSSION

The mechanism of the reduction of cyanide will be discussed in terms of three types of mechanisms usually proposed for permanganate oxidations. The first involves hydroxyl radicals, the second mechanism, one-equivalent oxidations by permanganate, and the third, a two-equivalent oxidation by permanganate giving hypomanganate as an intermediate. It will be shown that the mechanism involving hydroxyl radicals, mechanism I, is unimportant in the region of 0·07 M OH^- but makes an appreciable contribution at 0·48 M OH^-. The observed kinetics in the region of 0·07 M OH^- are consistent with either one- or two-equivalent oxidations by MnO_4^-, mechanisms II or III.

Mechanism I, involving hydroxyl radicals, is characterized by three one-equivalent redox steps. The first step is the reversible generation of OH·. The second step is the oxidation of CN^- by OH· yielding an intermediate X which is CN^- oxidized by one

Vol. 15 1960

equivalent. In the third step X then can be oxidized to CNO^- by another $OH\cdot$ or by a MnO_4^-. The origin of the cyanate oxygen is intimately connected with the formula of X. The oxygen could originate from the $OH\cdot$ consumed in second or third step or from the MnO_4^- in the last step. One possible mechanism using a specific X is illustrated below:

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + OH\cdot \quad (1)$$

$$OH\cdot + CN^- \rightarrow OH^- + CN\cdot \quad (2)$$

$$CN\cdot + OH\cdot \rightarrow CNO^- + H^+ \quad (3a)$$

or

$$CN\cdot + MnO_4^- \rightarrow CNO^- + MnO_3 \quad (3b)$$

$$MnO_3 + OH^- \rightarrow MnO_4^{2-} + H^+$$

If the rate determining step is the forward of reaction (1), the rate will be first order in both hydroxide and permanganate.

Mechanism I can only lead to a hydroxide ion dependent path and is certainly unimportant in the region of 0·07 M OH^-. However, run S does give evidence for the above hydroxyl radical path at higher OH^- concentrations. This is shown in this run by the enhanced rate and that the apparent rate constant increases during the run as the CN^- to OH^- ratio decreases. From run S we estimated that the ratio of the rate constants for the hydroxide to the cyanide path is $1 : 10^4$.

Mechanism II again involves a sequence of one-equivalent oxidations of CN^- resulting in CNO^-. It differs from Mechanism I in that the oxidizing agent for both redox steps of Mechanism II is MnO_4^-. X will be used to represent an intermediate containing carbon and nitrogen. A one-equivalent oxidation of CN^- yields X and a one-equivalent oxidation of X yields the same oxidation state as CNO^-. Mechanism II using specific formulas for possible intermediates, is illustrated below.

$$MnO_4^- + CN^- = MnO_4^{2-} + CN\cdot \quad (4)$$

$$MnO_4^- + CN\cdot \rightarrow MnO_3 + CNO^- \quad (5)$$

$$MnO_3 + OH^- \rightleftharpoons MnO_4^{2-} + H^+ \quad (6)$$

Mechanism III contains two two-equivalent redox steps. The first step is the oxidation of CN^- to CNO^- by MnO_4^- yielding hypomanganate. The second redox step is the reaction of manganese (VII) and (V) to give manganese (VI). This mechanism, involving hypomanganate, is illustrated below with specific formulas for the possible intermediates.

$$MnO_4^- + CN^- = MnO_3 + CNO^- \quad (7)$$

$$MnO_3^- + OH^- \rightarrow MnO_4^{3-} + H^+ \quad (8)$$

$$MnO_4^{3-} + MnO_4^- \rightarrow 2\,MnO_4^{2-} \quad (9)$$

A few remarks pertinent to these mechanisms are in order. First, it is known[8] that k_9 is very large. Second, the oxygen in permanganate does not exchange[9] with the solvent while the manganate oxygen does. Third, no information is available on

[8] A. Carrington and M. C. R. Symons, *J. Chem. Soc.* 3373 (1956).
[9] M. R. S. Symons, *J. Chem. Soc.* 3676 (1954).

oxygen exchange with the solvent for cyanate or hypomanganate. Fourth, partial oxygen transfer from MnO_4^- in the reduction by cyanide has been reported[10] but neither the conditions nor the resulting oxidation state were stated. The above mechanisms are consistent with oxygen transfer to the cyanate from the permanganate.

Thus the preliminary report of BRYCE and coworkers findings[10] of oxygen transfer cannot be used to distinguish between mechanisms II and III.

For both mechanisms II and III the overall activation energy has to be associated with the first step. For both mechanisms: $-d[MnO_4^-]/dt = 2k_A[CN^-]\,[MnO_4^-]$ where k_A is the specific rate constant for the forward rate of the first reaction [equations (4) or (7)] for both mechanisms. The first step of each mechanism is not inconsistent with a low activation energy since neither of these steps can be expected to be highly endothermic.

It may be concluded:

(1) in the region of 0·07 OH^- the experimental specific second-order rate constant is twice the specific rate constant for the elementary reaction between cyanide and permanganate and the experimental activation energy is to be associated with this elementary reaction,

(2) sodium ion has the same effect as potassium ion,

(3) at 0·5 M OH^- there is also a reaction path involving hydroxyl radicals.

[10] W. A. BRYCE, R. I. CARLSON and R. STEWART, ref. 2 private communication quoted by LADBURY and CULLIS, *Chem. Rev.* **58**, 403 (1958).

Vol. 15 1960

J. Inorg. Nucl. Chem., 1960, Vol. 15, pp. 377 to 383. Pergamon Press Ltd.

ION EXCHANGE BEHAVIOUR OF THE ACTINIDE ELEMENTS IN HYDROCHLORIC ACID

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(*Received* 7 *December* 1959)

Abstract—In an effort to confirm the earlier explanation for the elution pattern seen in this system, a greater range of actinide elements has been studied in several different batches of Dowex-50. Our results indicate that there is insufficient data at present to accept the earlier explanation as any more probable than several other possible suggestions.

THE study of the elution behaviour of the actinide elements from ion exchange resins has been one of the principal fields of research on those elements.[1] One reason for this is that ion exchange systems provide the basis for very practical separation schemes. However, since these systems allow the use of tracer levels of radio-isotopes—necessary in the case of transplutonium elements—and also provide exactly identical conditions for studying complicated systems, they can yield valuable information on the physical chemistry of the actinides. In particular, the complexing of these elements by various inorganic and organic anions have been investigated. In most cases the tripositive actinide elements show analogous behaviour to tripositive lanthanide elements; a notable exception to this is the hydrochloric acid elutions of these two families from Dowex-50 cation exchange resin first studied by STREET and SEABORG[2] and DIAMOND *et al.*[3] In the acid concentration range which they investigated (3–12 M), the lanthanides and actinides studied had comparable and steadily decreasing values for the resin-solution distribution constant (K_d) up to 6 M acid. Beyond this point the lanthanides stopped their steady decrease and began a slow increase while the actinides continued the decrease, although at a slower rate. The difference in the value of K_d between the lanthanides and the actinides in concentrated hydrochloric acid has resulted in the use of this solution as an eluant in an ion exchange separation of these two elemental families. The suggestion was made that this difference in the distribution constants, reflecting a greater degree of chloride complexing for the actinides than for the lanthanides, could be due to the involvement of 5*f* orbital sin the actinides in hybrid covalent bonds. In addition to the difference between the two families, the elution order of the actinides changed from curium–americium–plutonium

[1] G. R. CHOPPIN, *J. Chem. Educ.* **36**, 462 (1959).
[2] K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **72**, 2790 (1950).
[3] R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).

in dilute acid to plutonium–americium–curium in concentrated acid. A later investigation[4] in concentrated acid showed the order to be fermium–einsteinium–californium–berkelium–americium–curium. A possible explanation of this effect was offered by DIAMOND *et al.*[3], which again involved the utilization of the 5*f* orbitals.

Following DIAMOND's suggestion[5] that the difference between the complexing ability of the lanthanides and actinides should be even more pronounced with thiocyanate than with chloride, a detailed study was made of such a system by SURLS and CHOPPIN[6]. As predicted, the actinides showed greater complexing with thiocyanate than did the lanthanides; however, the elution order was normal for the actinides from Dowex-50, i.e. in inverse order to the atomic number, and followed no simple pattern for either the lanthanides or the actinides from Dowex-1 anion resin.

A careful investigation of the elution pattern of the tripositive actinides from plutonium through einsteinium as a function of hydrochloric acid was undertaken to extend the earlier studies to actinides not available at that time. In later publications, the results of similar studies of all the lanthanide elements and yttrium, scandium and actinium will be reported.

EXPERIMENTAL

1. *Ion-exchange resin column experiments*

Dowex-50 resins were used throughout this investigation. In some experiments spherical 4% D.V.B. resin was used while in the remainder, colloidal aggregates of 12% D.V.B. resin were used. The colloidal resin was of two different batches—one obtained in 1953 and the other in 1957. In all cases the resin was of the 200- to 400-mesh stock and the fraction that settled at the rate of 0·5 to 1·0 cm/min in water (approximately 18–25 μ) was used. Prior to use the resin was washed with hydrochloric acid, sodium hydroxide and, again, hydrochloric acid with water washes between each.

The actinides used were prepared by long time neutron irradiation of plutonium-239 in the Materials Testing Reactor.[7] The hydrochloric acid was prepared by passing hydrogen chloride gas through conductivity water until the solution was saturated, then diluting with conductivity water as needed.

The resin was packed into Pyrex glass columns of 0·1–0·3 cm internal diameter with the bed height varying from five to 10 cm. The particular set of diameter and length dimensions used depended on the concentration of acid eluant. After washing the resin bed with several millilitres of the eluant excess solution was removed from above the bed and the tracers added in one drop of eluant. The, glass walls of the column above the bed were washed after passage of the initial loading volume into the resin to remove unadsorbed tracers, and several millilitres of the eluant solution added to begin elution. The individual drops from the column tip were collected on platinum plates, dried under a heat lamp, ignited to remove any organic matter and counted in appropriate fashion. Rather slow rates (0·1–0·2 ml min^{-1} cm^{-2}) were used to obtain more symmetrical elution peaks by approaching equilibrium flow conditions. In the elutions with plutonium present, the solutions were made 0·1 M in hydroiodic acid to insure the presence of only plutonium (III).

^{241}Am, ^{244}Cm, ^{239}Pu, ^{252}Cf and ^{253}Es were counted in a 2π α-particle counter. To resolve this gross α-count into the contribution from each isotope in the broad elution peak, it was necessary to use a fifty-channel α-pulse-height analyser in which α-emitters may be identified by the characteristic energies of the α-particles. The β-particles from ^{249}Bk were counted in a windowless proportional counter. ^{252}Cf was counted in a spontaneous fission counter as well as in the α-analyser.

2. *Equilibrium experiments*

Weighted amounts (0·2–0·6 g) of Dowex-50 4 per cent resin in the hydrogen form were sealed in 15 ml tubes with known volumes (usually 3·0 ml of hydrochloric acid of varying concentration

[4] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 6229 (1954).
[5] R. M. DIAMOND, Thesis, University of California Radiation Laboratory Unclassified Report UCRL-1434 (1951).
[6] J. P. SURLS, JR. and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).
[7] S. G. THOMPSON, A. GHIORSO, B. G. HARVEY and G. R. CHOPPIN, *Phys. Rev.* **93**, 908 (1954).

Vol. 15 1960

containing tracer amounts of ^{244}Cm and $^{154,155}Eu$. After overnight agitation in a 25·0 ± 0·5°C bath to insure equilibration, the tubes were opened and 0·5 ml aliquots of the solution removed for titration and counting. The ^{244}Cm was counted on platinum plates in an α-counter while the europium was counted with an end-window Geiger-Muller counter. The titration was performed with sodium hydroxide. Duplicate samples of each concentration were run and the total concentration

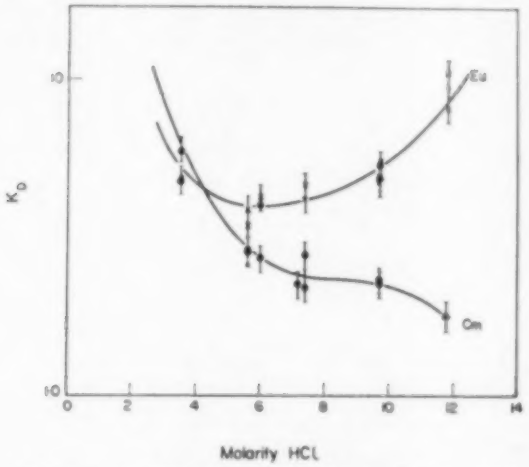

FIG. 1.—Logarithm of K_d vs. hydrochloric acid concentration for europium and curium.

range was covered in two sets of overlapping experiments for check purposes. It is worth noting that these are not ideal conditions for a static equilibrium measurement as at these concentrations and volumes of HCl with such relatively large resin weights the amount of water and electrolyte adsorbed by the resin will be significant.

RESULTS

The results of the equilibrium experiments are shown in Fig. 1. The K_d values were calculated from the expression:

$$K_d = \frac{C_T - C_S}{C_S} \times \frac{V_S}{W_R}$$

where C_T = counts per minute in 0·500 ml aliquot of solution before equilibration.
C_S = c.p.m. in 0·500 ml aliquot of solution after equilibration.
V_S = Volume of solution. (in ml)
W_R = weight of resin. (in g)

A typical elution curve after resolution into the component activities is presented in Fig. 2. The drop number corresponding to the maximum of the elution peak of each actinide ion is recorded in Tables 1 and 2 for various hydrochloric acid concentrations. No comparison should be made for these values at different acid concentrations as various column dimensions and drop volumes were used in order to effect elution in a reasonable volume. The peak was usually determined to one half of a drop by drawing a smooth, symmetrical shape for the top of the elution curve except in some cases where narrower (or broader) peaks allowed more (or less) precise values to be ascertained. In Table 2, the data "A" were obtained with a batch of 12 per cent crosslinked colloidal resin in 1954; the data "B" were obtained with at more

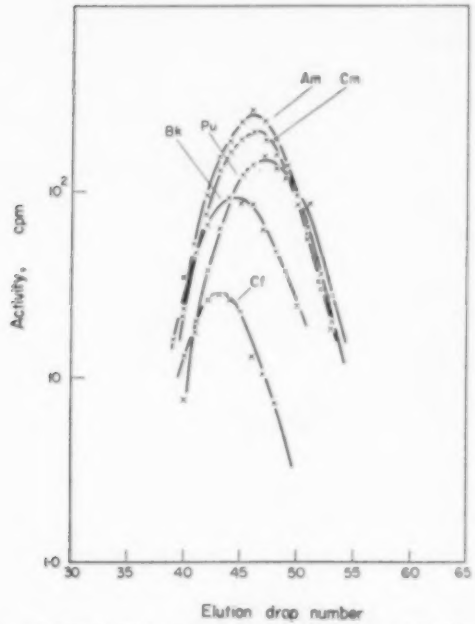

FIG. 2.—Elution of actinides from Dowex-50 with 9·7 M hydrochloric acid.

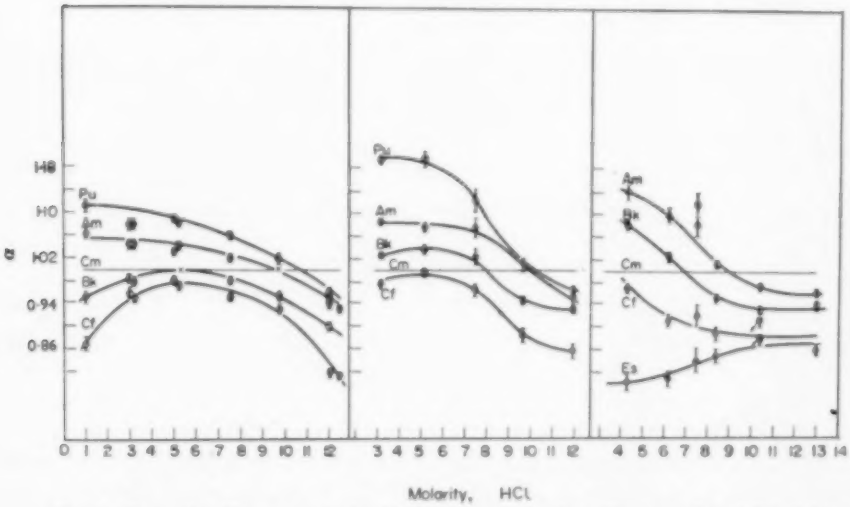

FIG. 3.—Separation factor, α, vs. hydrochloric acid concentration. The curves from left to right are for Dowex-50–4%, Dowex-50–12% (1954) and Dowex-50–12% (1957).

recent batch of the same type resin. Unfortunately, ^{253}Es tracer (20 day half-life) was not available for the later experiments (including the spherical resin).

Fig. 3 illustrates the behaviour of the actinides as separation factors (α) relative to curium such that

$$\alpha_M = \frac{\text{Drop number of elution peak maximum for M}}{\text{Drop number of elution peak maximum for Cm.}}$$

Vol. 15 1960

No corrections were made in the elution drop numbers for the "free column volume", i.e., the interstitial solution volume in the resin bed when elution began and which, therefore, did not contribute to the separation. This correction would not be significant for the data in Table 1 and the uncertainties in drop volumes, column diameters, etc. for that in Table 2 make the correction unfeasible. The correction would change

TABLE 1
(Dowex-50 4%)

Molarity HCl	Pu	Am	Cm	Bk	Cf
1·0	69	66	62	59	54
3·0	45·6	43·7	42·0	41·0	40·0
3·1	13·2	12·7	12·2	11·9	11·7
3·2	90·5	87·6	83·5	81·5	79·5
5·0	—	15·8	15·3	—	15·0
5·2	50·6	48·8	46·8	46·8	45·6
7·5	48·6	46·5	45·6	45·0	43·6
9·7	47	46	46	44	43
12·0	—	35·0	37·3	33·5	30·3
12·0	23·4	23·2	24·4	—	—
12·5	—	41·5	44·5	—	36·0

TABLE 2
(Dowex-50 12% Colloidal)

Molarity HCl	Pu	Am	Cm	Bk	Cf	Es
A: 4·3	—	74	65	70	63	52
6·2	—	43·5	39·5	40·5	36·0	32·0
7·5	—	28	25	27	23	21
8·4	—	23·3	23·5	22·3	21·0	20·0
10·4	—	15·0	15·3	14·2	14·0	13·5
13·0	—	15·6	16·3	15·3	14·0	14·0
B: 3·2	122·5	111·0	102·0	105·0	100·0	—
5·2	46·3	41·5	38·4	40·0	38·2	—
7·5	34·0	32·5	30·0	31·0	29·0	—
9·7	36·0	35·7	35·3	33·5	31·4	—
12·0	21·7	21·4	22·4	21·0	19·3	—

the shape of the curves in Fig. 3 somewhat but not to an extent to invalidate any conclusions to be drawn from them. The order of elution would remain the same in all cases. The error limits shown in Fig. 3 were calculated by assigning reasonable uncertainties in the drop numbers and calculating the resulting deviations relative in all cases to curium only. As a result, these limits are not to be regarded as expressing the uncertainty in relative position between berkelium and californium, for example, which would be less uncertain than indicated.

DISCUSSION

If the K_d curves for the 4 per cent resin in Fig. 1 are compared to those of DIAMOND *et al.*[3], for colloidal resin, keeping in mind that our data are for Eu and Cm whereas

the curves for colloidal resin are for Pm and Am, no large differences are seen. The K_d values for the 4 per cent resin are lower than for their colloidal resin but the shapes of the curves are quite similar. However, consideration of the separation factor data in Fig. 3 points up the necessity for caution in interpreting ion exchange data for only one resin type (or even one batch of resin) or only one eluant concentration where very small differences in selectivity are involved.

In Table 3, it can be seen that the abnormal order (Cf, Cm, Bk, Am, Pu) in moderate concentrations of HCl is seen for colloidal resin but not for 4 per cent spherical resin

TABLE 3.—ORDER OF ELUTION

Moderate HCl	(a) Cf–Bk–Cm–Am–Pu	4% resin
	(b) Cf–Cm–Bk–Am–Pu	12% colloidal resin
	(c) Es–Cf–Cm–Bk–Am	12% colloidal resin
Concentrated HCl	(d) Cf–Bk–Am,Pu–Cm	4% resin
	(e) Cf–Bk–Am–Pu–Cm	12% colloidal resin
	(f) Es,Cf–Bk–Am–Cm	12% colloidal resin

where the order is the usual one, i.e., the inverse order to the atomic number. Even for the two colloidal resins, a relatively large difference is seen in the relative separation factors (e.g. in 4 M HCl, 1·04 and 1·09 for Bk). Such variations due to the resin only are of the same magnitude as the "reversal" in concentrated acid. A similar behaviour was noted in the thiocyanate studies where the elution order in 3 M NH_4SCN changed from Am, Lu, Pm, from Dowex-50 4 per cent crosslinked resin to Lu, Am, Pm, from Dowex-50 12 per cent crosslinked resin.[6]

In an attempt to explain the reversal in elution order from Cm, Am, Pu to Pu, Am, Cm, as the concentration of hydrochloric acid is increased, it was suggested[3] that the 5*f* orbitals are "shrinking" or decreasing in their availability for utilization in bonding after plutonium. As a result, in strong acid, where presumably MCl_6^{3-} is formed, the order of complexing strength would be Pu, Am, Cm. The elution of berkelium and californium before curium in strong acid, again indicating stronger complexing for these two elements compared to curium, was attributed to a renewed availability of the *f* orbitals due to the smaller sizes of the berkelium and californium ions. While this earlier work reported that plutonium eluted slightly ahead of curium in 13 M HCl and in this study americium seemed to elute first, in both cases the differences are very small and it is felt that no real disagreement exists in the data.

If this suggested explanation is valid, the same trends would be expected to be seen in thiocyanate complexing but such was not the case. It is also necessary to reconcile the order, in moderate acid concentrations as shown in Table 3 for colloidal resin. In addition to this abnormal order, several other trends can be seen in the data presented in Fig. 3. In general Pu, Am, Bk and Cf all show a related behaviour which differs markedly from that of curium. Secondly, einsteinium does not follow this general behaviour but seems to be more like curium. Earlier studies[4] of actinide elutions indicated that fermium will be more like berkelium and californium, at least in concentrated acid. If the argument for renewed availability of *f* orbitals after curium accounts for the behaviour of berkelium and californium being more like americium and plutonium, it is logical to interpret the behaviour of einsteinium as meaning that

Vol. 15 1960

once again, as at curium, these orbitals have decreased in their availability and this effect has overcome the rate of decrease in ion size (actinide contraction). However, this should mean that fermium, einsteinium and californium should coincide or reverse in the same that plutonium, americium and curium do and, so far, this does not seem to be the case. Nor is there any obvious explanation for the "abnormal" order in moderate acid concentrations based on the *f* orbital concept.

The "reversal" in 3 M NH_4SCN between 4 and 12 per cent resin was interpreted as indicative of the importance of the exchange reaction:

$$M^{3+} + 3NR = MR_3 + 3N^+ \text{ (R = resin anionic site)}$$

in such small effects. The data presented in Fig. 3 seem also to confirm the idea that the exchange reaction is at least of the same magnitude of importance as complexing strength effects in the reversals observed. A further point made in the article on thiocyanate complexing that is worthy of repeating is the fact that the difference in free energies involved in the complex formation between americium and curium for example, is on the order of only 100–200 cal. Such small energy differences could be due to effects which are regarded as insignificant in less sensitive systems. The differences in polarizability of the cations has been suggested as one such effect. This effect would be quite sensitive to the rate of change of the ionic radius. It is probable that there is an interruption in the smooth rate of contraction at the ion with a half-filled *f* shell, Cm^{3+}. The deviation of curium from the pattern of the other actinides is observed also in elution with other eluants (Fig. 8, ref. 4). A number of possible explanations for this behaviour were suggested in that reference.

SUMMARY

The more complete investigation reported here of the actinide–hydrochloric acid–cation resin system seems to raise objections to the earlier interpretation of the elution order in concentrated acid in terms of *f* orbital hybridization alone. A number of other explanations for these elution sequences have been suggested but it is not possible with the present data to choose a unique one. This question and interpretation of the details of the elution orders of the tripositive actinides, lanthanides and Group III A elements in these systems will be discussed in subsequent publications. However, the data and arguments presented here do not contradict the *f* orbital interpretation of the much larger difference between the lanthanide and actinide families in concentrated hydrochloric acid.

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NOTES

A novel method for the preparation of carrier-free lead-212[1]

(*Received* 9 *May* 1960)

CARRIER-FREE lead-212, a member of the naturally occurring thorium-232 series, has been prepared by collecting the active deposit from highly emanating thorium oxide samples[2] and by the sweeping of thoron from thorium nitrate solutions with a stream of air.[3] In the procedure reported here a nitric acid solution of thorium nitrate is refluxed in a Soxhlet extractor in which the usual extraction thimble is replaced by a small (22 × 55 mm) cation-exchange resin column. The thoron which escapes from the boiling solution is carried along with the vapours into the upper part of the apparatus where the water vapour condenses; it is in this region that the thoron collects and decays to polonium-216 which in turn decays to lead-212; the lead-212 is subsequently washed onto and retained by

TABLE 1.—DEPENDENCE OF RECOVERY OF LEAD-212 FROM AQUEOUS THORIUM NITRATE SOLUTIONS ON TIME OF REFLUX[a]

Time of reflux (hr)	Activity on resin (%)	Activity in condenser, (%)
3·7	1	24
6·1	2	29
15·1	3	21
42·4	21	12

[a] 575 ml of 0·065 M $Th(NO_3)_4$ was refluxed in a 1 l. flask.

the resin. In order to prevent the escape of thoron from the apparatus into the laboratory, the condenser is sealed with Parafilm after most of the air in the apparatus has been displaced by water vapour (about 2 min after refluxing has begun). The lead activity is eluted from the resin and removed from the walls of the condenser with 1 N hydrochloric acid; the resulting solution may be used directly or evaporated to dryness in a quartz crucible under a heat lamp and subsequently dissolved in a dilute strong acid or acetic acid.

The results of several experiments are summarized in Tables 1, 2 and 3. The yield was essentially independent of reflux times less than 15 hr (Table 1), decreased slightly with increase in volume of the solution (Table 3), and was only slightly dependent on the nitric acid concentration; the yield was highest (~45%) for a nitric acid concentration of 1 M (Tables 2 and 3). It is noteworthy that when a pure thorium nitrate solution was used most of the activity was found on the walls of the

[1] The research presented in this communication was sponsored by Sandia Corporation under P.O. No. 51-6541.
[2] E. M. MORIMOTO and MILTON KAHN, *J. Chem. Educ.* **36**, 296 (1959).
[3] E. BRODA, H. FABITSCHOWITZ and T. SCHONFELD, *Monatsh.* **83**, 482 (1952).

Vol. 15 1960

condenser (Table 1); when the acidity of the thorium nitrate solution was increased by addition of nitric acid, a greater percentage of the activity was found on the resin. This behaviour may be correlated with the relatively high pH (~5) of the condensate of a pure thorium nitrate solution compared with that (pH = ~2) of thorium nitrate solutions, 1 M in nitric acid.

Solutions of lead-212 in equilibrium with its decay products, were counted with a scintillation detector employing a sodium iodide (thallium activated) crystal and a No. 5819 R.C.A. phototube. The percent recovery was based on the lead-212 activity separated from a known amount of thorium nitrate in equilibrium with its decay products; the growth and decay of lead-212 in the apparatus

TABLE 2.—EFFECT OF NITRIC ACID CONCENTRATION ON RECOVERY OF LEAD-212 FROM THORIUM NITRATE SOLUTIONS[a]

Volume of soln. (ml)	$Th(NO_3)_4$ conc. (M)	HNO_3 conc. (M)	Activity on resin (%)	Activity in condenser (%)
575	0·065	0·014	22	14
575	0·065	0·014	10	17
580	0·065	0·14	26	11
580	0·065	0·14	37	6
625	0·060	1·3	40	5
625	0·060	1·3	41	5
675	0·055	2·38	33	6
675	0·055	2·38	34	5

[a] Average time of reflux = 10·8 ± 0·2 hr.

TABLE 3.—DEPENDENCE OF RECOVERY OF LEAD-212 FROM AQUEOUS THORIUM NITRATE SOLUTIONS ON VOLUME OF SOLUTION[a]

Volume of soln. (ml)	Volume of boiling flask (ml)	Activity on resin (%)	Activity in condenser (%)
50	100	36	15
50	100	37	11
250	500	32	8
500	1000	28	3

[a] Average time of reflux = 12·0 ± 0·5 hr; $Th(NO_3)_4$ concentration = 0·75 M; HNO_3 concentration = 1 M.

was taken into account in these calculations. This separation was effected by the precipitation of lead carrier from a thorium nitrate solution with hydrogen sulphide; the sulphide was washed with 0·1 N nitric acid, dissolved in 2·5 N nitric acid, diluted to 0·1 N nitric acid with water and again precipitated with hydrogen sulphide. The final precipitate was dissolved in 2·5 N nitric acid and diluted for counting. Dowex-50 cation-exchange resin, acid form, 8 per cent cross linkage, 100–200 mesh, obtained from Bio Rad Laboratory, was further purified by treatment with 6 N hydrochloric acid and subsequently washing with water. The thorium content of a thorium nitrate solution was checked by employing a gravimetric procedure based on the precipitation of thorium oxide.[4]

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[4] C. J. RODDEN (Editor), *Analytical Chemistry of the Manhattan Project*. NNES, Vol. VIII, Div. 1, p. 183. McGraw-Hill, New York (1950).

Chemical behaviour of phosphorus-32 recoils in crystalline disodium hydrogen phosphate*

(*Received* 7 *June* 1960)

THE chemical behaviour of recoil phosphorus in inorganic crystalline systems has been repeatedly investigated.[1-13] LIBBY[1] examined the radiophosphorus formed by the n, γ reaction in several hydrated alkali phosphates. Two fractions were distinguished, ^{32}P which precipitated with magnesium ammonium phosphate and the residuum, oxidized with bromine and then similarly precipitated, and thought to contain phosphite. The relative insensitivity of the phosphate yield (retention) to changes in environment of the recoils, led LIBBY to conclude that the initial recoil determined the retention, subsequent reactions having no effect on the oxidation state. Later work[4,5,6,8] drew specific attention to the formation of recoil species containing more than one phosphorus, for example, pyrophosphate.

Two recent papers by SELLERS *et al.*[10,13] reported the ^{32}P yields from irradiations *in vacuo* of various inorganic crystalline phosphorus compounds. Their separation technique (paper electrophoresis) gave results which indicated that in all cases virtually all the ^{32}P activity was present as the parent compound.

Earlier work of BORLAND *et al.*[8] however, had shown that high neutron flux and ambient temperature during neutron irradiation of KH_2PO_4 as well as thermal annealing after irradiation produced an almost complete conversion of the non-orthophosphate fraction into orthophosphate. Such annealing effects might explain the discrepancy between the work of SELLERS *et al.*[10,13] and the workers cited above. In addition, studies of phosphorus recoil in inorganic sulphur and chlorine compounds had suggested that in lattices containing hydrogen in any form (crystal water, NH_4^+ etc.) lower oxidation states of ^{32}P should be expected.[11]

We have recently engaged in an extensive study of ^{32}P recoil reactions in crystalline systems as a function of radiation and thermal environment, i.e. temperature of bombardment, flux, neutron to gamma ray ratio, annealing conditions, and crystalline environment. Our results do not agree with those of SELLERS *et al.*[10,13] that the principal recoil reactions are the production of labeled parent forms. Like them, we employed paper electrophoresis separations. In Fig. 1 is shown a typical histogram (activity vs. distance along strip). The salt was anhydrous Na_2HPO_4 bombarded at dry ice temperature† for 30 min at 2×10^{13} n/cm² sec, Cd ratio about 40. This salt was dissolved in ice-cold 0·1 M lactic acid, and 5–10 λ analysed by electrophoresis on a strip of Whatman 3 MM moistened with 0·1 M lactic acid, at a voltage gradient of 80 V/cm for about 1 hr. We have determined the per cent activity, and tentatively identified the peaks labeled in the histogram, as follows:

A tripolyphosphate, 12·2%
B pyrophosphate, 11·7%
C unknown, probably two species, 12·0% total
D isohypophosphate, 27·1%
E hypophosphate, 2·8%
F orthophosphate, 9·3%
G diphosphite and possibly another species, 7·7% total
H phosphite, 8·2%
I hypophosphite, 6·8%

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† This bombardment was made with the sample sealed in quartz, in the presence of air. Parallel experiments with samples sealed in quartz in high vacuum gave nearly identical results.

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Vol. 15 1960

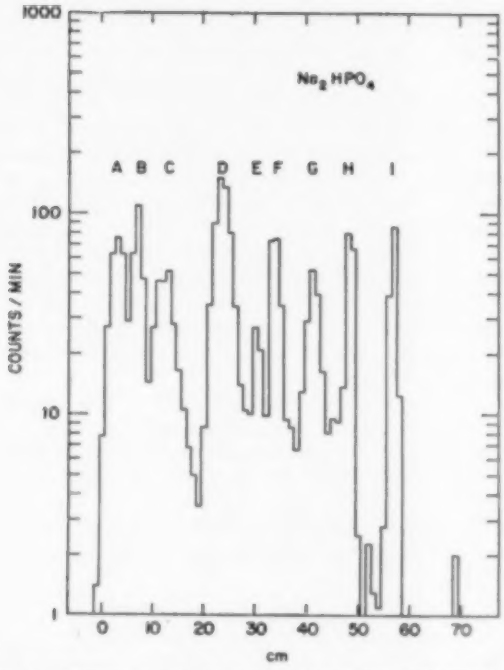

FIG. 1.—Electrophoresis histogram of neutron-bombarded Na_2HPO_4. Radioactivity vs. distance.

When the above irradiation conditions were varied by increasing the ambient temperature of bombardment our results began to approach those of SELLERS *et al.* These changes confirmed our belief that annealing during and/or after bombardment may have influenced their results.

We therefore believe that their conclusion, that "neutron irradiation of the various phosphates did not produce extensive disruption of the P—O bonds or the P—O—P linkages"[18] is unjustified. We believe, on the contrary, that the maximum probability of non-bond-rupture in crystalline phosphates is not greater than our observed orthophosphate percentage, namely 9·3 per cent, and may well be lower.

We will report our complete results on a number of such crystalline phosphorus systems shortly.

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Diphenoxysilicon phthalocyanine[1]

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THE recent preparation of several germanium phthalocyanines[2] suggests that similar silicon phthalocyanines may exist. A successful method for the preparation of one of these diphenoxysilicon phthalocyanine, has been developed. The first step in the synthetic sequence used for this compound,

[1] This work was supported in part by a grant from the Research Corporation of America.
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the reaction between phthalonitrile and silicon tetrachloride, varies from a previously attempted synthesis of silicon phthalocyanines in which use was made of metal free phthalocyanine and silicon tetrachloride.[3]

Experimental

Repeated treatment of a refluxing mixture of 26 g of phthalonitrile in 50 ml of quinoline with 85 g of silicon tetrachloride over a 4 hr period produced a black tarry mixture. Separation of this mixture gave a dark solid which after washing with acetone and dimethyl sulphoxide yielded 1 g of a purple crystalline product. The similarity of the infra-red spectrum of this material to the spectrum of dichlorogermanium phthalocyanine[3] indicated that it was probably dichlorosilicon phthalocyanine. After refluxing 0·3 g of these crystals (further purified by a pyridine wash) for 3 hr with 20 ml of an equal volume mixture of pyridine and concentrated ammonia, a blue material was obtained, which because of the great similarity of its infra-red spectrum to that of dihydroxygermanium phthalocyanine, was assumed to be dihydroxysilicon phthalocyanine. Treatment of this product with 1·5 g of molten phenol and five drops of pyridine followed by cooling and washing with benzene gave diphenoxysilicon phthalocyanine.

Sublimation of 0·25 g of the diphenoxysilicon phthalocyanine thus obtained at 360°C and a pressure of 2 μ for 2½ hr onto a collecting finger maintained at 260°C by refluxing chloronaphthalene, yielded 75 mg of well formed crystals ,which were blue-green by transmitted light and reddish-purple by reflected light. (Found: C, 73·19; H, 3·84; Si, 3·81. Calc. for $C_{44}H_{26}SiO_2$: C, 72·71; H, 3·61; Si, 3·86.)

The infra-red spectrum of this compound was very similar to that of its germanium analogue. As expected it showed an absorption in the region for monosubstituted benzenes (at 701 cm^{-1}).

Discussion

It is noteworthy that the spectrum of what was presumed to be dihydroxysilicon phthalocyanine showed one strong peak which was not present in the spectrum of dihydroxygermanium phthalocyanine. This absorption was at 832 cm^{-1} and may have been due to the SiOH grouping.[4]

The silicon phthalocyanines represent a departure from the behaviour generally associated with the element silicon and the phthalocyanine ring in that most phthalocyanines are formed with elements that are considerably more metallic than silicon. In addition the silicon atoms in these compounds may be assumed to be bound to four planar nitrogen atoms and to two other atoms, one above and the other below the plane of the ring; an arrangement of bonds which is not usual for silicon. The diphenoxy compound is of particular interest in that it again demonstrates the feasibility of bonding groups to the central element with oxygen bridges[2] and the general importance of the inorganic functionality of the phthalocyanines.

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Vol. 15 1960

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Comparison of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope effects in some reactions of hydrogen peroxide

(*Received* 24 *June* 1960)

At a time when it appeared that the $^{14}C/^{13}C$ isotope effect in the decarboxylation of malonic acid was more than twice the $^{13}C/^{12}C$ effect, Pitzer and Gelles made the suggestion[1] that catalysis by the nuclear magnetic moment of ^{13}C might account for the discrepancy. The later work of Yankwich

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et al.[1] showed that the ratio of the two effects is, in fact, 1·91 ± 0·17. Therefore, if the PITZER effect exists for the malonic acid reaction, it is either too small to be observed or there is no spin change involved in forming the activated complex.

It was considered desirable to look for such an effect in oxygen since ^{17}O has a nuclear magnetic moment but ^{16}O and ^{18}O do not. Furthermore, many reactions of oxygen do involve a spin state in the activated complex different from that of the reactants. Therefore the $^{18}O/^{16}O$ effect might not be twice the $^{17}O/^{16}O$ effect. Reactions chosen for this study were some oxidations and reductions of hydrogen peroxide. The method used was that of CAHILL and TAUBE[2] except that $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios were measured in the same sample. The results are shown in Table 1 together with

TABLE 1

Reagent	Reaction	Number of determinations	f^{18}	R^*	f^{18} (CAHILL and TAUBE)
Fe^{++}	Reduction	3	0·954	2·05 ± 0·01	0·933
I^-	Reduction	2	0·947	2·06 ± 0·03	0·945
Cl_2	Oxidation	2	0·995	1·8 ± 0·3	0·990
MnO_4^-	Oxidation	2	0·999	2·1 ± 0·4	

* $R = \dfrac{1 - f_{18}}{1 - f_{17}}$

fractionation factors reported by CAHILL and TAUBE. It should be noted that there is a spin change during the net change for all reactants except iodide ion.

The values of R are generally more consistent than separate values of f^{18} or f^{17}. Thus for Fe^{++} f^{18} varies from 0·943 to 0·967 (which is not in good agreement with the results of CAHILL and TAUBE) while R varies only from 2·04 to 2·06. The most likely sources of error were (1) interference by catalytic decomposition and (2) incorrect determination of the fraction of hydrogen peroxide used up. Neither of these affects R as long as f^{18} and f^{17} are determined in the same sample. Values of f were more consistent in the other systems. However, in the oxidizing systems the isotope effect is so small that one cannot attach a great deal of significance to the values obtained.

Since the values of R are in all cases close to 2, there is no indication of a difference between the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope effects that is not explained by mass differences. Thus, if there is any catalytic effect due to ^{17}O, it is too small to be observed in the systems studied.

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A list of some of the papers to be published in future issues

J. B. CORBETT and W. J. BUCKARD: Pressure–composition data for the liquid HCl–HBr system at dry ice temperature.

S. P. RANDALL and J. L. MARGRAVE: Vapour equilibria in the B_2O_3–H_2O system at elevated temperature.

E. L. MUETTERTIES, T. A. BITHER, M. W. FARLOW and D. D. COFFMAN: Chemistry of phosphorus fluorides.

W. E. KEDER: Neptunium complex ion species extracted from nitric acid–perchloric acid mixtures by tributyl phosphate.

R. RÄTZ and C. GRUNDMANN: Tri- and tetra-meric phosphonitridic fluoride.

W. V. CHILDS and E. S. AMIS: A study of transference and solvation phenomena—II. Silver perchlorate in water, water–ethanol, and ethanol solvents.

F. K. LOTGERING: Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures—II.

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N. S. GILL, R. H. NUTTALL, D. E. SCAIFE and D. W. A. SHARP: The infra-red spectra of pyridine complexes and pyridinium salts.

Vol. 15 1960

E. L. SHORT and D. F. C. MORRIS: Zinc chloride and zinc bromide complexes—I. Cation exchange studies with zinc-65 tracer.

T. J. COLLOPY and J. J. KLINGENBERG: Spectral evidence for zirconium–mandelic acid complexes in ethanol.

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